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Chemical Residues in Fish Tissues in Alberta

II. Mercury in the North Saskatchewan River

ENVIRONMENTAL CENTRE

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CHEMICAL RESIDUES IN FISH TISSUES IN ALBERTA

II. Mercury in the North Saskatchewan River

Alberta Environmental Centre

Vegreville, Alberta

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SUMMARY

(1) Total and methyl mercury were determined in several species of fish, sediment, and water samples from the North Saskatchewan River from upstream of Edmonton to the Saskatchewan border.

(2) Total mercury in goldeye averaged 0.57 mg/kg whereas the corresponding levels for walleye, sauger and pike were 0.56, 0.59 and 0.31, respectively.

(3) Using a Maximum Tolerable Weekly Intake of 0.25 mg for a 50 kg adult, approximately 440g (~16 oz) of goldeye flesh can be consumed per week, regardless of fish size.

(4) No consumption standards need to be placed on walleye or pike measuring < 35 and 60 cm in length respectively. However, Maximum Weekly Intake of 380 g (~13 oz) should be applied to larger fish of both species.

(5) Due to the sensitivity of the developing fetus to mercurials, pregnant women should not consume fish from the North Saskatchewan River.

(6) There is no apparent anthropogenic or geologic source of mercury in the Alberta portion of the North Saskatchewan River. Based on sediment and water analysis, industrial and municipal discharges from Edmonton do not contribute significantly to the burden. It is possible that the former use of mercury as a fungicide still

constitutes a non-point mercury discharge source. However, since the most heavily contaminated fish in the river are migratory, it is more likely that uptake occurs in Saskatchewan where there are several possible sources (pulp/paper mills, chlor-alkali plants, Tobin reservoir, gold dredging).

(7) Studies have been initiated by the Alberta Environmental Centre to determine

(i) the movement of fish from Alberta and Saskatchewan

(ii) mercury residues in fish, sediments and water collected from the Saskatchewan portion of the river

(iii) energetics of goldeye and walleye in relation to migration and mercury uptake

(iv) the presence of metalloproteins in fish as a detoxifying agent.

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1. INTRODUCTION

The health hazards of environmental mercury are well documented in the literature. The consumption of mercury contaminated fish resulted in neurological illnesses and even deaths in Japan. This was the first known modern case of hazards of environmental contamination by mercury. The disease became known as Minamata Disease and was traced to methylmercury contamination of the Minamata Bay from effluents from chemical manufacturing (PVC) factories. Several other alarming incidents from other parts of the world revealed other sources of mercury contamination such as fungicides from pulp and paper mill, seed dressing chemicals and effluents from chlor-alkali plants. Additional non-point discharge sources of mercury include runoffs from agricultural land treated with mercury-containing fungicides for decades before being banned in early 1970's.

By 1930, organic mercury compounds for seed dressing were introduced in Canada. In the 1940's the use of mercurials for seed treatment was most popular in Western Canada and about 95 agricultural chemicals (containing 18 different mercury compounds) were registered for sale in Canada. It has been estimated that about 75% of cereal crops in Alberta in 1960's were treated with mercurials and about 60-120 tons of elemental mercury in the form of organomercury compounds entered in the soils of Saskatchewan during 1930-1972 (Fehr and Dennis, 1975). Seed-eaters and their avian predators (hawks, falcons, and owls) of Alberta were reported to have contained higher mercury residue levels (23%) than their counterparts in Saskatchewan (4%) (Fimreite et al, 1971).

Elevated levels of mercury in some species of fish in the surface waters of Alberta have been reported earlier (Sherbin, 1979). Only total mercury values were reported, lacking the important information about the fraction of methyl mercury which is several times more neurotoxic than inorganic mercury. Also, the data collected range over a period of ten years during which analytical methodology was continuously being refined to improve the quality and the limit of detection. Hence it is difficult to place an estimate of quality on the existing data on a relative basis. No data exist on the mercury levels in sediments, an important compartment in the mercury flux in the environment. Hence the Aquatic Biology Group developed the method for the analysis of inorganic, methyl and total mercury in environmental samples.

Sources of Mercury Contamination

Natural sources:

Major natural sources of mercury in the aquatic environment are from:

(i) soil degassing and subsequent wet or dry precipitation

(ii) weathering and erosion of rocks and mineral deposits

(iii)volcanic activity.

It has been estimated that (NAS, USA, 1977) 60-65% of the atmospheric mercury burden is from natural sources.

Anthropogenic sources:

Table 1 lists the variety of industrial end-use categories of mercury and the demands of mercury for each category. The projected

Table 1. Actual and projected demand (in USA) for mercury by industrial categories.

(metric tons)

Category	1974[a]	1985[b]	2000[b]	2025[b]
Chlorine and caustic soda	582	511	0	0
Paint	235	265	244	355
Pesticides	34	18	21	27
Catalysts	45	46	58	70
Pharmaceuticals	21	27	38	36
Instruments	173	172	142	180
Tubes, switches and relays	60	82	86	213
Batteries	613	650	787	1028
Lamps	47	68	114	179
Dental	104	89	100	115
Laboratory	16	18	21	27
Cther	121	127	159	139
Total	2051	2073	1770	2369
		(1323)[c]	(1153)	(1540)
		(3055)[d]	(2604)	(3531)

Sources: [a]Cammarota (1975); [b]Watson (1979); [c]Low estimate; [d]High estimate.

figures clearly show that mercury will continue to be used in industrial applications well beyond this century.

Table 2 summarizes the Canadian production and consumption of mercury during 1967-1976 (George, 1977).

(i) Release from chlor-alkali plants:

Chlor-alkali plants produce chlorine, caustic soda, sodium hypochlorite and hydrochloric acid. Plants using the mercury cell release large amounts of mercury containing wastes mostly in sludge (approximately 200 mg/kg of Hg). The sludge is concentrated in settling ponds and deposited in local landfills (van Horn, 1975). Estimates have shown that the runoffs from these landfills (even after retirement of the mercury cell operation) pose a serious environmental problem. Replacement of mercury cells by diaphragm cell plants will meet the water discharge regulations for mercury. It is hoped that by 1985 almost all mercury cells would have been replaced by diaphragm cells. A revised chlor-alkali Mercury Liquid Effluents Regulations (Canada Gazette, Part II, 1977) established a maximum discharge rate of 2.5 g of mercury/day/metric ton of chlorine produced.

(ii) Release from discarded mercury-containing goods:

Consumption and discarding of goods that contain mercury such as pharmaceuticals and dental analyses constitute a large percentage of discharge of mercury to water. Other discharges via land use the goods placed in the landfill sites. These goods are thermometers, electrical tubes, switches, relays, primary batteries, lamps and mercury vapor tubes. It is estimated that this source of mercury discharge will

Table 2. CANADIAN MERCURY PRODUCTION, TRADE AND CONSUMPTION 1967-1976 (Geogre, 1977).

	Production Metal	Imports Metal	Consumption Metal
		(kilograms)	
1967	-	161 615	111 185
1968	195 117	89 766	148 751
1969	727 380	60 600	140 076
1970	841 141	69 536	154 474
1971	637 750	55 338	87 982
1972	504 581	79 243	51 998
1973	430 912	48 171	32 959
1974	482 622	108 817	37 786
1975	413 676	73 524	32 869[1]
1976[P]	-	62 638	26 039[1]

Sources Statistics Canada for all figures, except for metal production statistics, obtained directly from Cominco Ltd. and representing output from its Pinchi Lake mine in B.C.

[P] Preliminary; - Nil

[1] Partial consumption only.

continue to be the largest source even beyond this century (Watson, 1979). Abrasion or destruction of dental amalgam is calculated to release approximately 150 kg/yr for one urban centre of population of 1 million (Sherbin, 1979).

(iii)Release from fuel burning and scrubbing:

A low megawatt coal-burning plant using 360 tonnes per hour of coal (containing 0.5 mg of Hg/kg) emits 180 g of mercury per hour substantially to the air. Scrubbing captures the mercury in the scubbing sludges which are deposited in landfills. Thus scrubbing is likely to shift the impact of mercury discharges from air to land and eventually to water. Canada in 1974, consumed 22,857 kilotonnes of coal (Statistics Canada, 1975) and based on an average Hg content of 0.1-0.3 mg/kg (HMSO, 1976; Jonasson, 1970) this would amount to 2.3-6.9 tonnes of Hg release per year. Similarly, using a mean value of 0.3 mg/kg of Hg in fuel oils, (aviation fuel, gasoline, diesel oil, etc) a yearly mercury emission of 18 metric tons has been calculated for Canada (Environment Canada, 1973).

(iv) Release from pulp and paper mills:

Mercury compounds were used in pulp and paper industries as a preservative for the pulp and as a slimicide in the paper mills. Substantial amounts of mercury-containing effluents were released from the pulp and paper industries leading to environmental problems in the receiving waters. In 1970, all Canadian pulp and paper companies stopped using mercurials. Although this has resulted in eliminating

mercury inputs into water, the slow release from the past residues in sediment near discharge sites could still pose an environmental threat.

(v) Release from mercury-containing pesticides:

By 1930, organic mercury compounds for seed dressing were introduced in Canada. In the 1940's the use of mercurials for seed treatment was most popular in Western Canada and about 95 agricultural chemicals (containing 18 different mercury compounds) were registered for sale in Canada. It has been estimated that about 75% of cereal crops in Alberta in the 1960's was treated with mercurials and about 60-120 tons of elemental mercury in the form of organomercury compounds entered in the soils of Saskatchewan during 1930-1972 (Fehr and Dennis, 1975). Seed-eaters and their avian predators (hawks, falcons and owls) of Alberta were reported to have contained higher mercury residue levels (23%) than their counterparts in Saskatchewan (4%) (Fimreite et.al, 1971). Agricultural runoffs from lands containing residues of these mercury-containing fungicides would result in low-medium level but widespread contamination of the aquatic system.

(vi) Release from mining and smelting operations

Mining and smelting operations release mercury-containing particulates in their wastewaters. Base metal smelters and refineries also release mercury in their wastewaters. Annual mercury releases from zinc, copper and lead production were estimated to be 8 metric tons in Canada (Environment Canada, 1973). Most of the mercury present in the base metal ores ends up in the concentrates (2-150 mg/kg in the zinc concentrates; 0.02-15 mg/kg in the copper concentrates). Relatively

lower amounts of Hg appear in mine tailings (MacLatchy and Jonasson, 1974).

(vii)Release from municipal wastewater treatment plants:

Effluents, digested sludges from the municipal wastewater treatment plants and the sediments around the discharge area are reported to be relatively high in mercury concentrations. About 50% of the mercury in the municipal wastewaters originates from disposals from hospitals, dentists, and laboratories. About 25% is from mercury using industries and the rest is made up of human wastes and natural contamination (EPA, 1975). A survey of mercury in sewage sludges in Southern Ontario showed a range of 1 mg/kg (rural) and 26 mg/kg (heavy urban). Processed sludge fertilizers contained up to 10 mg/kg of Hg while inorganic fertilizer contained less than 0.4 mg/kg of Hg (van Loon, 1973).

Role of sediment in mercury dynamics in the aquatic environment

On entry into surface waters, mercury is quickly depleted from the water phase and immobilized in the natural sinks, namely sediments. Mercury associates with the sediments through several possible interactions:

(i) ion exchange
(ii) complexing or chelation with organic matter
(iii)sorption onto colloids of ferromanganese oxides and
(iv) incorporation into the crystal lattices of the mineral grains.

Sediment is a complex mixture with four main components: silica, clays, organic matter and oxides of iron and manganese. Thus the

association of mercury with sediments could range from weak van der Waals forces to strong covalent bonding. Studies on the sorption capacities of river sediments (Ramamoorthy and Rust, 1976; 1978) revealed that high bonding energy constant and the sorption maximum (refer equation 1) account for the substantial capacity of the sediment to bind mercury:

$$c/x/m = (1/kb) + (c/b) \quad \ldots\ldots\ldots\ldots\ldots \quad 1$$

where c=equilibrium concentration of the sorbate (Hg), x/m=amount of sorbate per unit mass of the sorbent (sediment), k=a constant related to the bonding energy of sediment for Hg and b=sorption maximum. The parameters k and b of the Langmuir's equation (1) correlated directly with organic content and grain size of the sediment.

The release of the sorbed Hg from the sediment into the bulk water is dependent on the partition coefficients, which in turn are related to the sediment characteristics, type of heavy metal and other environmental parameters such as pH, presence of natural and/or synthetic chelating agents in water. Thus no sediment can be an "absolute sink" and the desorption may be a slow process, posing a long-term problem even after the sources of pollution are eliminated.

Interconversion of mercury in the environment

The facile interconversion of mercury in the environment is illustrated in Figure 1.

Speciation of mercury is a primary factor in determining its behaviour and fate in aquatic systems. It is important to identify the species and their rate of interconversion in natural waters since different physico-chemical forms of mercury have different resident

times and toxicological properties on fish and ultimately the human health. Recognition of the possible influence of metal speciation on the transport and bioaccumulation of mercury has stimulated detailed studies on the various aspects of mercury speciation in natural waters.

Mercury exists in three valency states; Hg^0 (elemental), Hg^+ (mercurous) and Hg^{2+} (mercuric) states. The nature and concentration of the species depends upon the pH, E_h (redox potential), and presence of complexing ligands. Thus in natural waters, the speciation of metallic mercury is given by the equation (2):

$$E = 850 + 30 \log \left(\frac{[Hg^{2+}]}{k}\right)$$

where E = minimum potential (mv) necessary for conversion of Hg^0 to Hg^{2+}

$[Hg^{2+}]$ = concentration of free Hg^{2+} ions,

k = binding constant between inorganic mercury and the chelators. Higher the k, the lower is the E necessary for conversion of Hg^0 to Hg^{2+} species. For example, for a k value of $10^{14.25}$ (Hg - cysteine chelate; Sillen and Martell, 1971) and for a concentration of $[Hg^{2+}]$=2 ppm(mg/l), the E necessary for total conversion of all forms of Hg to Hg^{2+} is 280 mv, much lower than the theoretical value of 850 mv. Natural waters contain enough organic and inorganic ligands and the redox potential of most fresh surface waters are around 500 mv. In fact, the k for Hg - organic mud has been calculated to be 10^{21} (Werner, 1967). Thus regardless of the state of the valence of mercury introduced into the aquatic system, it will be quickly converted to the Hg^{2+} species which is the most active species in binding to ligands through covalent binding. The Hg^{2+} ion undergoes either biological or abiological alkylation to produce an important group of organo mercuric compounds.

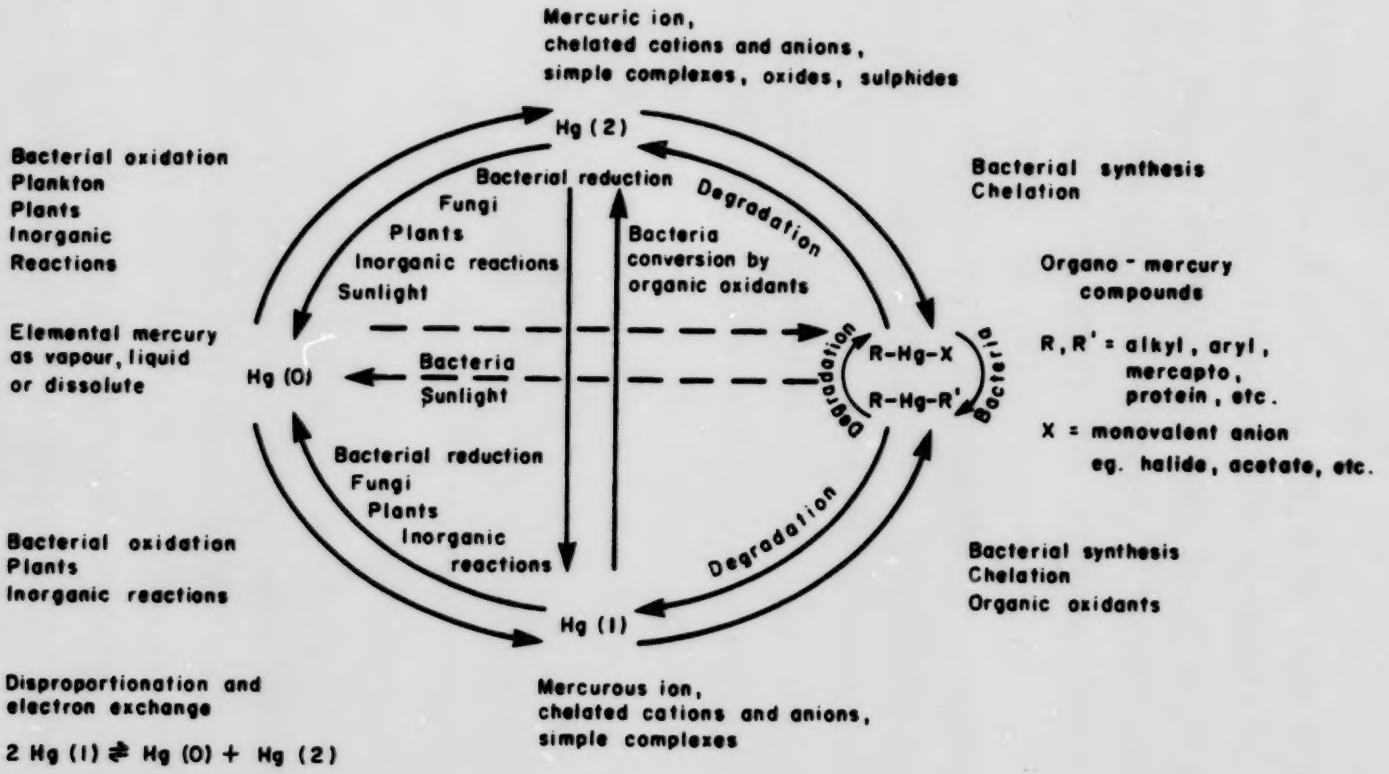


Figure 1. Interconversions of Mercury in the Environment.

These compounds could be either (i) [R-Hg-X (x=inorganic ligand, commonly Cl^-, OH^-, nitrate or sulphate anions)] or (ii) [R-Hg-R (R=alkyl (commonly methyl) or aryl (commonly phenyl) radical)]. The first (i) category is characterized by its ampiphilicity (soluble in both water and lipid) and persistence in aquatic system. The second (ii) category is non-polar, almost insoluble in water and extremely volatile. Biological methylation could be enzymatic or non-enzymatic but requires a methyl donor and free Hg^{2+} species. Many biological end products commonly found in natural waters are potential methyl donors. Types of bacteria have been identified to decompose methyl mercury (Spangler et al., 1973; Bartlett et al., 1977). Recently, the studies on the transformation of methyl mercury in water (Ramamoorthy et. al, 1982) have shown that the physiological state of the microorganisms present in the natural waters can greatly influence the Hg speciation and the amount of toxic Hg compounds present. In addition, sorption of Hg compounds by the particulates complicates the behaviour of mercury and its bioaccumulation pattern.

Toxicology of Mercurials:

From the toxicological point of view, mercurials are classified into several groups such as elemental mercury, inorganic mercury compounds other than elemental mercury, short-chain alkyl mercurials (methyl and ethyl) and other organomercury compounds (Friberg and Vostal, 1972; Suzuki, 1977). Dose-effect and dose response relationship have been studied and interpreted according to this classification (Suzuki, 1979). For methylmercury poisoning the critical organ is the brain for most animal species including man.

The polarity of the bio-complexes of Hg^{2+} and CH_3Hg^+ and their ampiphilicity contribute substantially in transport across membrane barriers inter- and intra-cellular distribution and accumulation in organs. The toxicology of alkyl and aryl mercurials reflect their coordination chemical properties. The extreme affinity of methylmercury for sulphur ligands, especially for deprotonated sulphydryl (-SH) groups accounts for its toxicity; inhibition of large number of enzymes, alteration or disruption of catalytic activity due to substitution of zinc atoms, distortion of the configuration of nucleic acids. The neurotoxic effect of CH_3Hg^+ is believed to be due to disruption of the lipid layers of the membranes of central nervous system cells (Segall and Wood, 1974). Inspite of the enormous amount of literature on mercury toxicity, it has not been proven unequivocally (i) to relate neurological disorder to the binding amino acid and (ii) the role of mercury binding metallothionein in sequestering CH_3Hg^+ especially when the order of affinity of thionein is $Hg^{2+} > Cd^{2+} > CH_3Hg^+$. Hence it is essential to understand the chemistry of these sequestering proteins at the molecular level in delineating the complex biological behaviour of mercury. Mercury problem on the whole involves many factors, including origin and persistence of mercuric compounds in water, their speciation, transformation into more toxic forms, bio concentration in fish (which is dependent on species, sex and age) and the continuous daily intake of mercury - contaminated fish in large quantities. At lower level but long-term intake, the subclinical effects on the general populations are more difficult to evaluate and thus become a serious human health threat.

2. METHODS AND MATERIALS

2.1 Fish

(i) Sampling sites:

The collection of fish, water and sediment samples from the North Saskatchewan River commenced in 1981. Figure 2 shows some major surface waters in the province of Alberta.

(ii) Sampling techniques:

Six collection trips were made during May 4 to June 2, 1982 to collect various fish species from the mouth of the Sturgeon River and its confluence with the North Saskatchewan River, about half a mile stretch (Figure 3). Samples were also taken from the Mrynam and Lea Park areas. Fish were collected using a 9 metre beach size, 2-28 metre multi-panel gillnets with equal lengths of 2.5, 5.0, 7.5 and 10.0 cm mesh size and also by angling.

A total of 159 fish were collected comprising nine species (Walleye, Sauger, Goldeye, Northern Pike, Longnose Sucker, Northern Redhorse Sucker, Quillback Sucker, White Sucker and Ling).

(iii)Sample preservation and handling:

Fish collected were placed on ice soon after capture and transported to the laboratory within six hours of capture and frozen to $-20^{o}C$. The whole fish was then slowly thawed and samples of muscle, fat, liver and gonad were taken from each fish. Structures such as scales, fin rays, opercular bone etc. depending on the fish species were also removed for ageing. Fork lengths and weights were recorded.

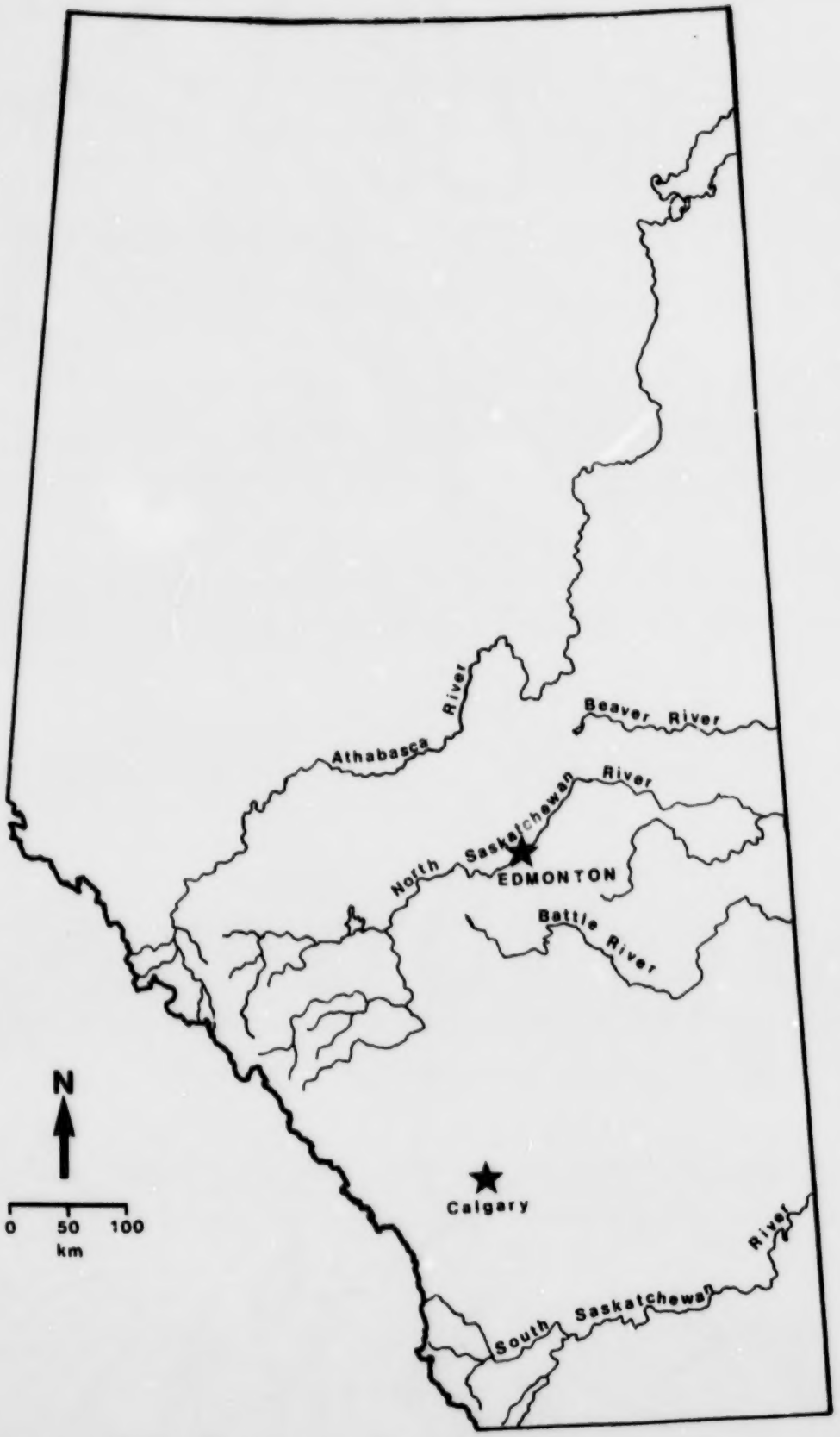


Figure 2. General map of the water bodies in Alberta

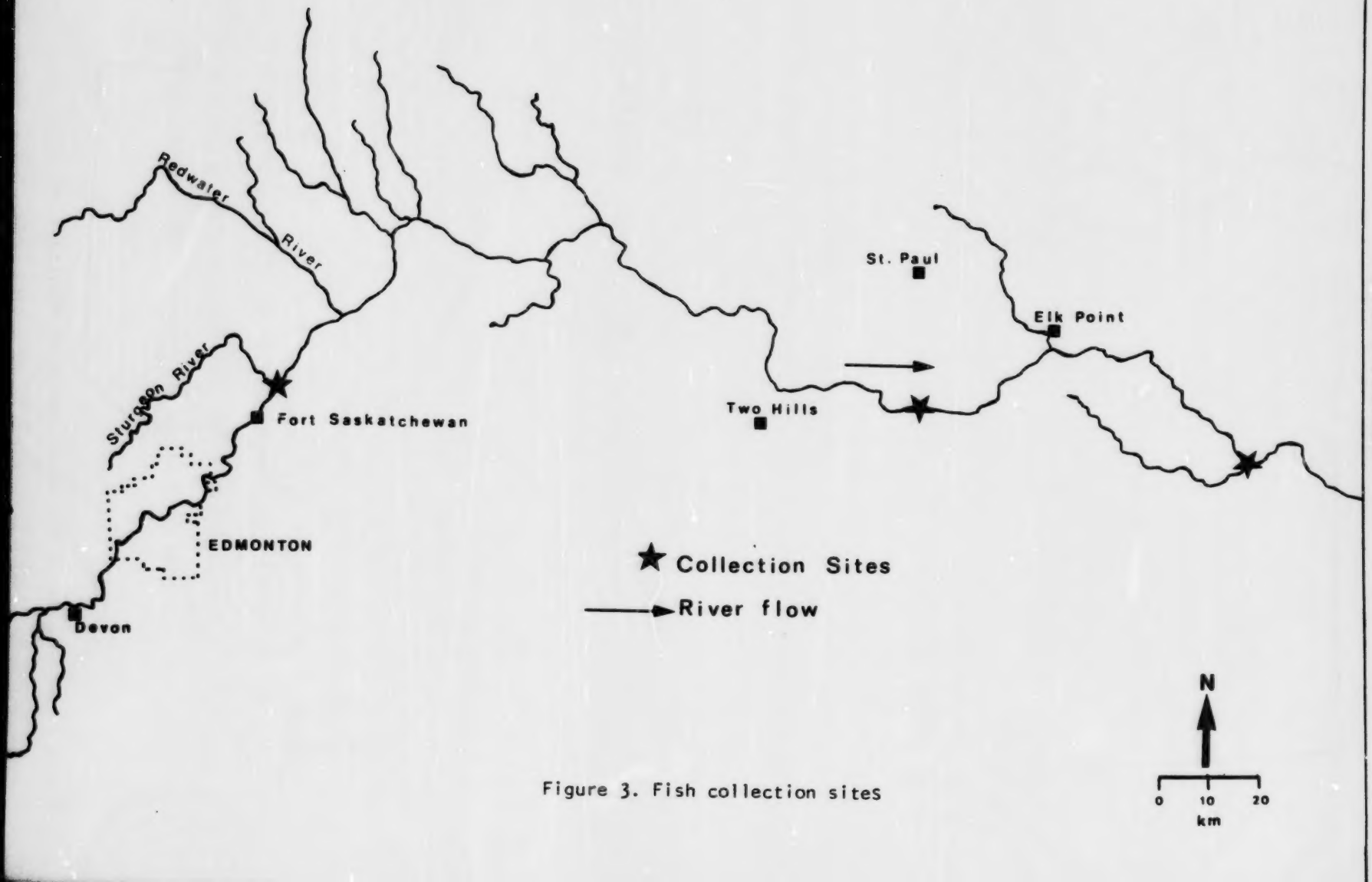


Figure 3. Fish collection sites

Muscle samples were taken from fillets and fat samples from the abdominal cavity usually along the intestine and from around the stomach. These samples were weighed, wrapped in foil, labelled, placed in Whirlpak® bags and frozen to -20°C until further chemical analysis.

(iv) Analytical methods:

Apparatus:

1) LDC (Laboratory Data Control, U.S.A.) Mercury Monitor equipped with a mercury hollow cathode lamp emitting monochromatic light at 253.7 nm (Figure 4).

2) Long path dual gas cell assembly (30 cm long and 0.75 cm diameter) made of rigid PVC with quartz lens windows at both ends.

3) Chart recorder.

4) Specially designed and constructed pyrex glass mercury reduction-bubbler assembly.

5) Pure Nitrogen gas source (Standard cylinder) with two-stage exit regulator for constant gas delivery at low flow rate.

6) Constant temperature shaker bath with gable cover, platform and clips to hold 20 or more glass digestion tubes, with a total capacity of 24-35 litres of water.

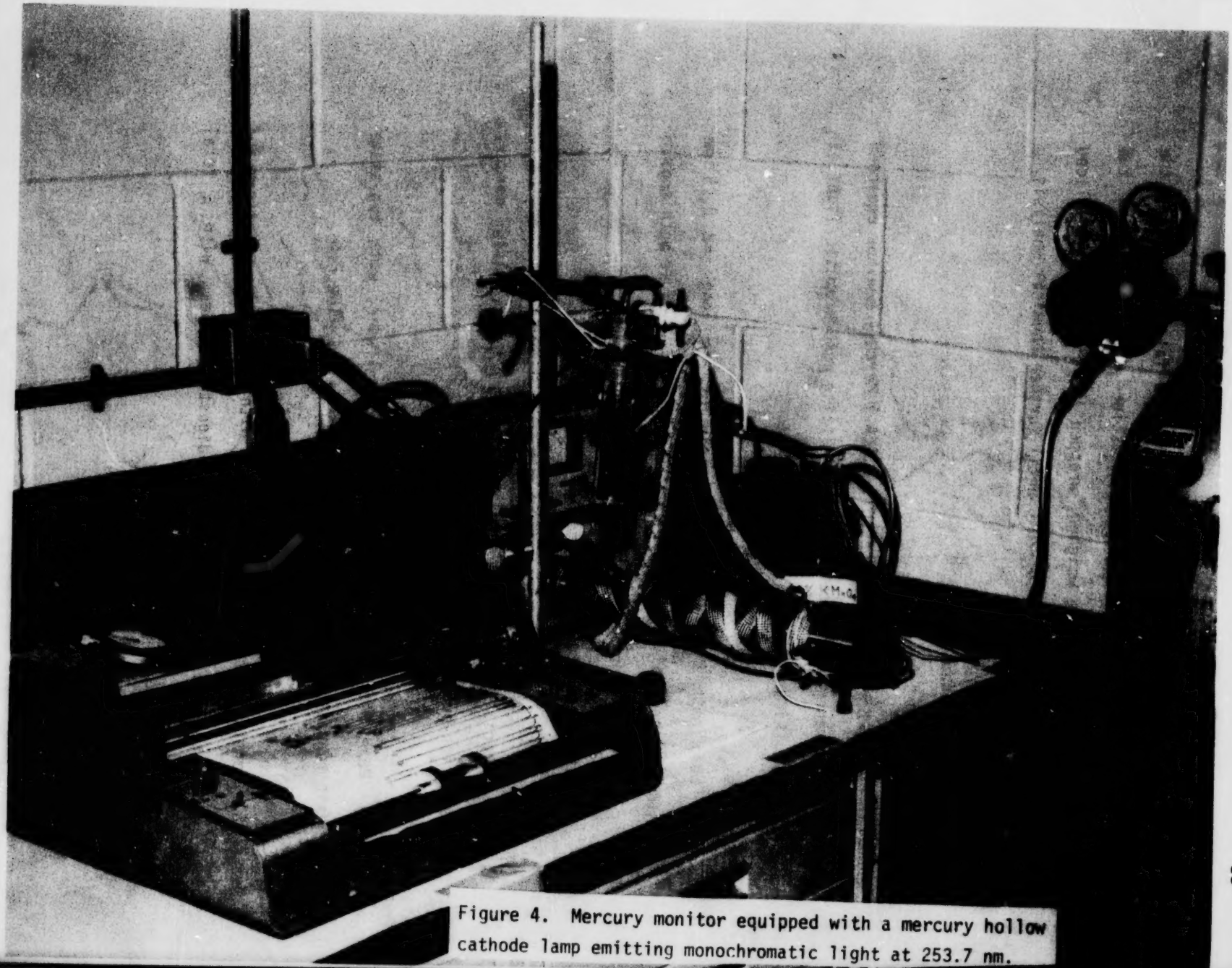


Figure 4. Mercury monitor equipped with a mercury hollow cathode lamp emitting monochromatic light at 253.7 nm.

7) Millimatic dispensers.

8) Pipetman and disposable tips.

9) Stop watch.

10) Magnetic Stirrer.

11) Homogenizer; sorvall omni-mixer, Polytron PT10 or standard electrical blender with special mini-blending jars.

Method:

a) Chemistry: The differential digestion method is applicable for the mercury determination in a wide variety of animal tissues. Aliquots of the sample are digested separately with (i) cysteine mixture (cysteine, Cl^- and 50% H_2SO_4) and (ii) strong acid mixture (conc. HNO_3 and H_2SO_4) and oxidant ($KMnO_4$) at 55-60°C to yield Hg (and CH_3Hg) - cysteine complexes and Hg^{2+} ions respectively. The two differently digested samples are then reduced with $SnCl_2/NH_2OH$ solution to determine the inorganic mercury in (i) and total mercury in (ii) respectively.

(i) Inorganic mercury analysis:

The cysteine-digested sample is reduced with a strongly alkaline $SnCl_2/NH_2OH$ solution and the Hg^0 produced is swept by pure N_2 gas into an absorption cell of the Mercury Monitor. Methylmercury is not reduced in this step.

a) $Hg\text{-cysteine} \xrightarrow[SnCl_2/NH_2OH]{OH^-(excess),\ Cl^-} Hg^0\uparrow + Sn^{4+}$

b) $CH_3\text{-}Hg\text{-cysteine} \xrightarrow[SnCl_2/NH_2OH]{OH^-(excess),\ Cl^-}$ No reduction

(ii) Total mercury analysis:

The sample digested with a mixture of strong acids and oxidant ($KMnO_4$) contains all the mercury (both inorganic and methyl mercury) in the Hg^{2+} form. The sample is reduced with strongly alkaline $SnCl_2/NH_2OH$ to determine the total mercury content.

a) $CH_3\text{-}Hg$ (and R-Hg) $\xrightarrow[H_2SO_4+HNO_3+KMnO_4]{-e} Hg^{2+}$

b) $Hg^{2+}_{total} \xrightarrow[SnCl_2/NH_2OH]{+2e} Hg^0\uparrow + Sn^{4+}$

Methylmercury analysis:

The difference in the values for a given sample for inorganic mercury (i) and total mercury (ii) gives the methyl mercury content of the sample. The flow diagram for a typical mercury analysis using LDC Mercury Monitor is given in Figure 5.

b) Sample preparation:

About 15g of fish muscle tissue free from bone and fat was blended with 7.5 ml of 0.1N H_2SO_4 in a stainless blending cup till a smooth paste was obtained. Some fish like Goldeye required only

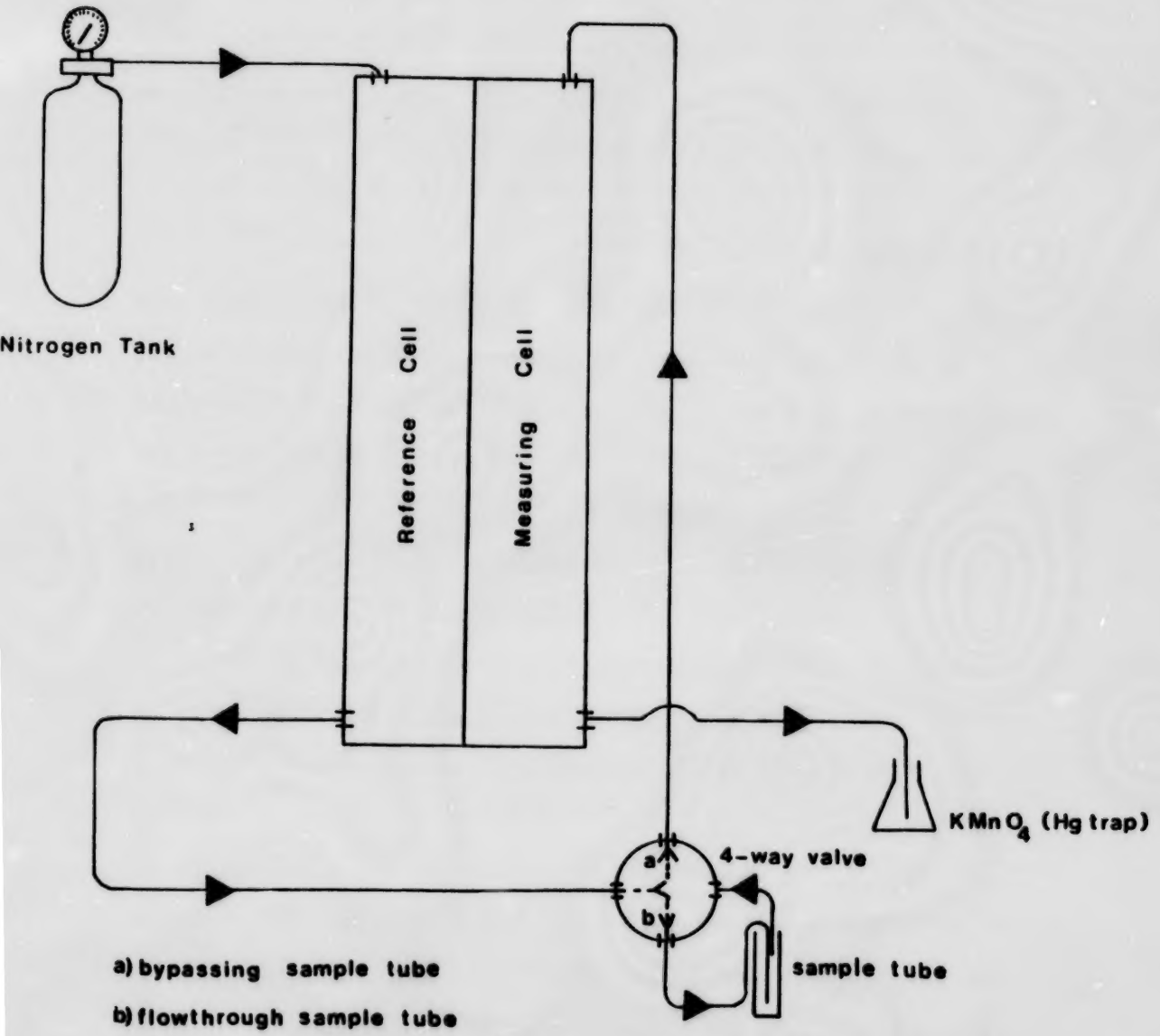


Figure 5. Flow Diagram for Mercury Analysis.

5.0 ml of 0.1N H_2SO_4 due to its higher water content. Usually 30 seconds of blending time was sufficient to produce a homogeneous paste.

Around 1 gm of the wet homogenate was weighed accurately into four digestion tubes. One aliquot was weighed into a petri dish and left loosely capped in a forced-air oven for 24h at 55°C to determine the wet/dry weight ratio. If a delay (more than 1 day) in analysis is anticipated, the aliquots were stored at -20°C in polypropylene cups sealed with lids.

c) Sample digestion:

(1) To two of the four aliquots in the digestion tubes, the following digestion mixture was added; 1 ml of 20% NaCl solution, 1 ml of 1% cysteine solution and 10 ml of 16N H_2SO_4. The tubes were tightly stopped in a shaker water bath at 55-60°C for 1 hr. Thorough mixing was ensured by adjusting the shaking speed. If the samples were not completely dispersed after 1h, they were shaken for an additional 0.5h. The tubes were then removed from the bath and cooled to room temperature. The sides and the stopper of the tubes were rinsed down with minimum d.d.w. (distilled deionized water) and made up to a known volume. The digested solutions were analyzed within 24h.

(2) To the remaining two aliquots in the digestion tubes, 5 ml of the digestion acid mixture (100 ml of conc. HNO_3 + 400 ml of conc. H_2SO_4) was added. The tubes were stoppered tightly, fitted into a rack and shaken in a water bath at 55-60°C for 2h or until a clear solution is obtained. The tubes were removed from

the bath and cooled to room temperature. 15 ml of 6% $KMnO_4$ solution was added slowly and allowed to stand for 30 min. If the purple colour disappeared at this stage, more $KMnO_4$ was added till the color persisted. Then 30% H_2O_2 solution was added with caution while stirring until the precipitate just dissolved. The solutions were made to a known volume and mixed well. The solutions were analyzed within 24h.

d) Calibration and analysis:

Stock (100 mg/l) intermediate (220 µg/l) and working standard solutions (0.1 - 1.0 µg/l) of inorganic mercury ($HgCl_2$) and total mercury ($HgCl_2$ and CH_3HgCl) were prepared.

Inorganic mercury analysis

(i) 15 ml of inorganic mercury standard was pipetted into the digestor-analysis tube.

(ii) 1 ml of 20% NaCl solution, 1 ml of 1% cysteine solution and 3 ml of 16N H_2SO_4 were added to the standard.

(iii) The tube was placed in position with the bubbler and flushed with N_2 gas to remove any interferring vapors.

(iv) 1 ml of $SnCl_2/NH_2OH$ solution and 2 ml of 45% NaOH solution was added in quick succession.

(v) After 30 seconds (using a stop watch) the mercury vapor produced was flushed by pure N_2 gas into the Mercury Monitor and the peak absorbance was recorded.

(vi) When the absorbances begin to decline, the 4-way valve was turned into bypass position and the bubbler tube was rinsed off.

(vii) The next standard solution was analyzed following steps (i) to (vi).

(viii)The blanks (all reagents except mercury) are analyzed as above to detect any blank interference.

(ix) Digested blanks and standards are also analyzed to detect any artefact introduced during digestion stage.

(x) All the samples digested for inorganic mercury analysis (sample digestion (1)) were analyzed following steps (i) to (vi).

Total mercury analysis:

(i) Exactly 15 ml of total mercury standard solution is pipetted into a digestor-analysis tube.

(1) 5 ml of the digestion acid mixture (con. HNO_3 + conc. H_2SO_4, 1:4 ratio) was added to the standard solution.

(2) The tubes were stoppered tightly, fitted into a rack and shaken in a water bath at 55-60^{o}C for 2h or until a clear solution was obtained.

(3) The tubes were removed from the bath and cooled to room temperature.

(4) 15 ml of 6% w/v $KMnO_4$ solution was added and allowed to stand for 30 min. If the purple color disappeared, more $KMnO_4$ solution was added till the color persisted.

(5) A solution of 30% H_2O_2 was added cautiously with stirring until the precipitate just dissolved.

(6) The solution was made up to a known volume and mixed thoroughly.

(7) The total mercury was analyzed by following the steps iii to ix as described under (d) for inorganic mercury analysis.

(8) All the samples digested for total mercury analysis (sample digestion (2)) were analyzed following steps (4) to (7) as described above.

e) Calculations:

After correcting for blank readings, if any, the calibration curves for inorganic and total mercury were prepared by plotting the peak heights (p.H.) versus the amount of Hg (Figure 6). The sample peak heights were compared with the respective calibration curves to determine the inorganic and total mercury concentrations. The differences between the inorganic and total mercury for the given sample is its methylmercury content. The amount of Hg per gram (wet weight) is given by:

$$\frac{\text{Amount of Hg (inorganic/methyl), } \mu g}{\text{*wet weight of subsample}} = \text{Amount of Hg (inorganic/methyl)}$$

*Since acid is added during homogenizing the tissue, the aliquoted wet weight was corrected to arrive at the true wet weight of the fish tissue in the sample. For example, when aliquots were taken

from a homogenate of 15 g of muscle tissue and 7.5 g of 0.1N H_2SO_4, the correction factor was 0.67. That is, every 1 g of wet aliquot contained only 0.67 g of wet fish tissue.

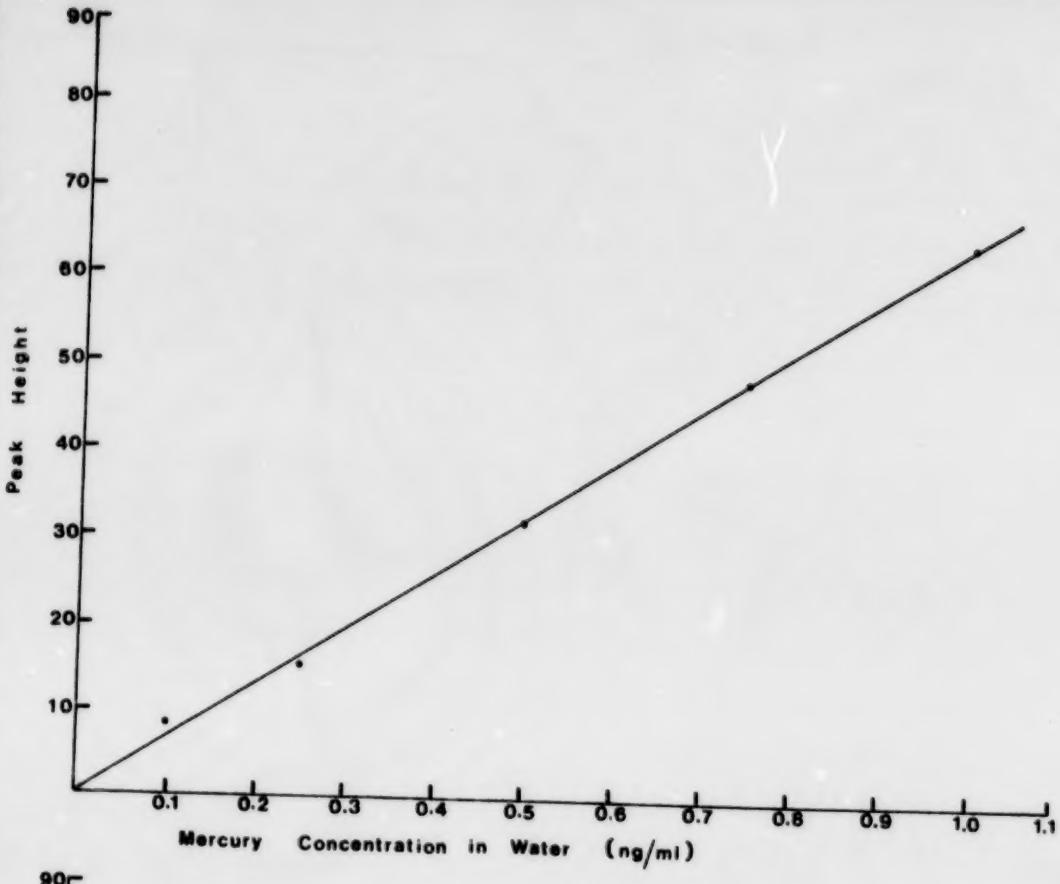
2.2 Sediment

(i) Sampling sites:

The North Saskatchewan River was divided into four sampling zones (A, B, C, and D) based on the discharges from land-runoffs, storm sewers, municipal and industrial discharges and agricultural land runoffs.

Zone A covered the section of the North Saskatchewan River between the Devon Bridge (upstream of Edmonton) and the 109th Street Bridge located in central Edmonton (Figure 7). This zone comprised mainly of input from storm sewers and land-runoffs. Sediment samples were collected every 0.5 km along this zone of the river where boat access permitted.

Zone B covered the section of the North Saskatchewan River from the 109th Street Bridge and the Fort Saskatchewan Highway Bridge (Figure 7). This zone of the river is characterized by input from municipal sewage outfalls, discharges from Refinery Row and other industrial activities.



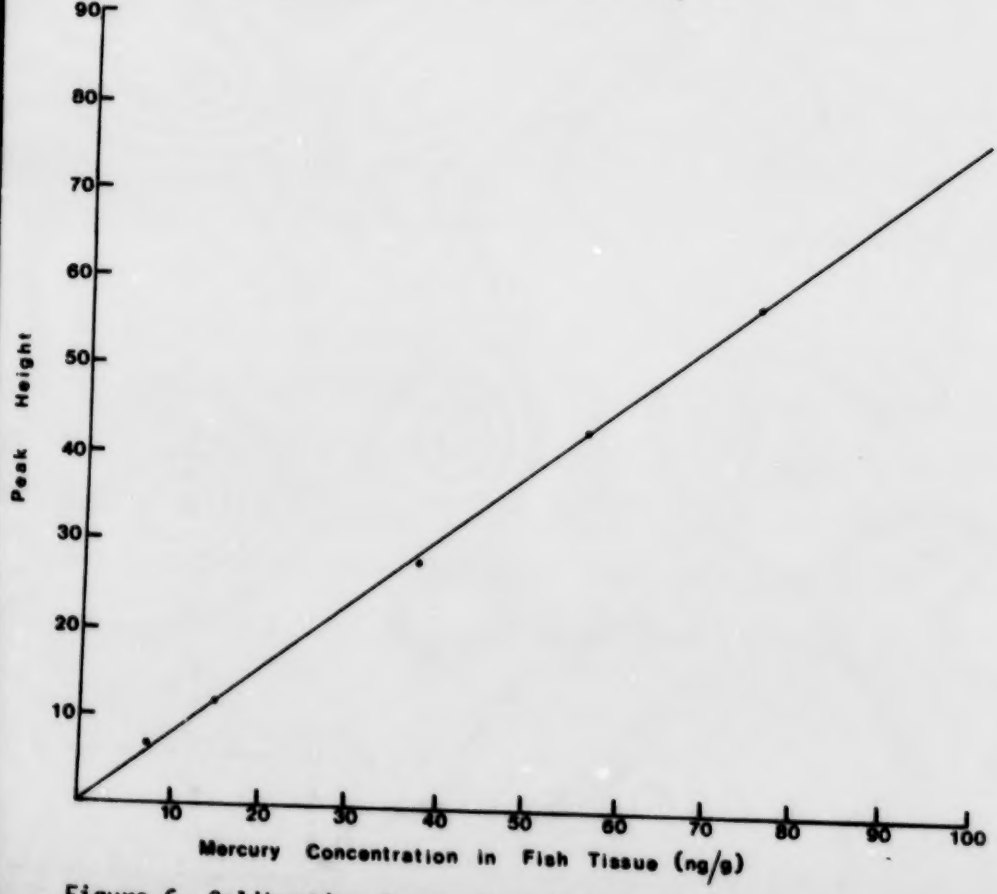


Figure 6. Calibration Curve; Peak Height vs Concentration

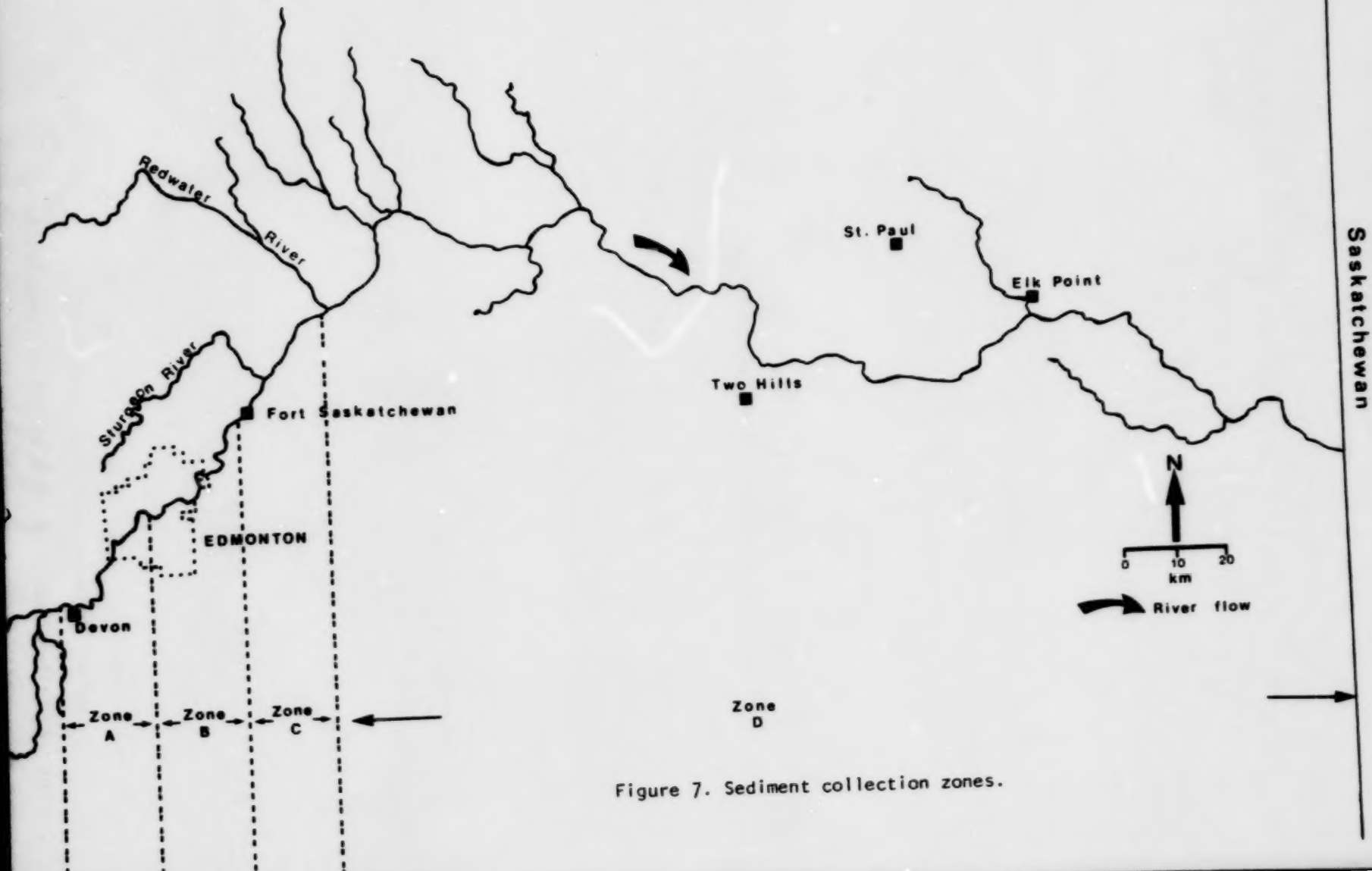


Figure 7. Sediment collection zones.

Zone C covered the section of the river from the Fort Saskachewan Highway Bridge to the Vinca (Redwater) Bridge (Figure 7). This zone of the North Saskatchewan River receives discharges from chemical industries and base metal refining and fertilizer manufacturing industries, located in Fort Saskatchewan. Sediment samples from Zones B and C were taken from those sites which permitted vehicle access.

Zone D covered the section of the river from the Vinca Bridge (Redwater) to the Alberta - Saskatchewan interprovincial border (Figure 7). This zone of the North Saskatchewan River receives input mainly from agricultural runoffs only. Sediments were sampled every 0.5 km along the length of this zone, depending upon the accessibility by boat.

(ii) Sampling techniques:

Bottom sediment samples were obtained using an air-lift suction sampler powered by the flow of compressed nitrogen gas at 250-450 psi (Figure 8). The surface layer (1 to 2 cm) of the bottom sediment was collected at 0.5 to 1.0 metre water depths where the air-lift suction sampler performs at maximum efficiency. In order to regulate the sampling depth, a base plate was attached to the cover to support the unit gently on the surface of the sediment. This enabled the sampler to maneuver the unit so that only the top 1 to 2 cm of bed sediment was sampled.

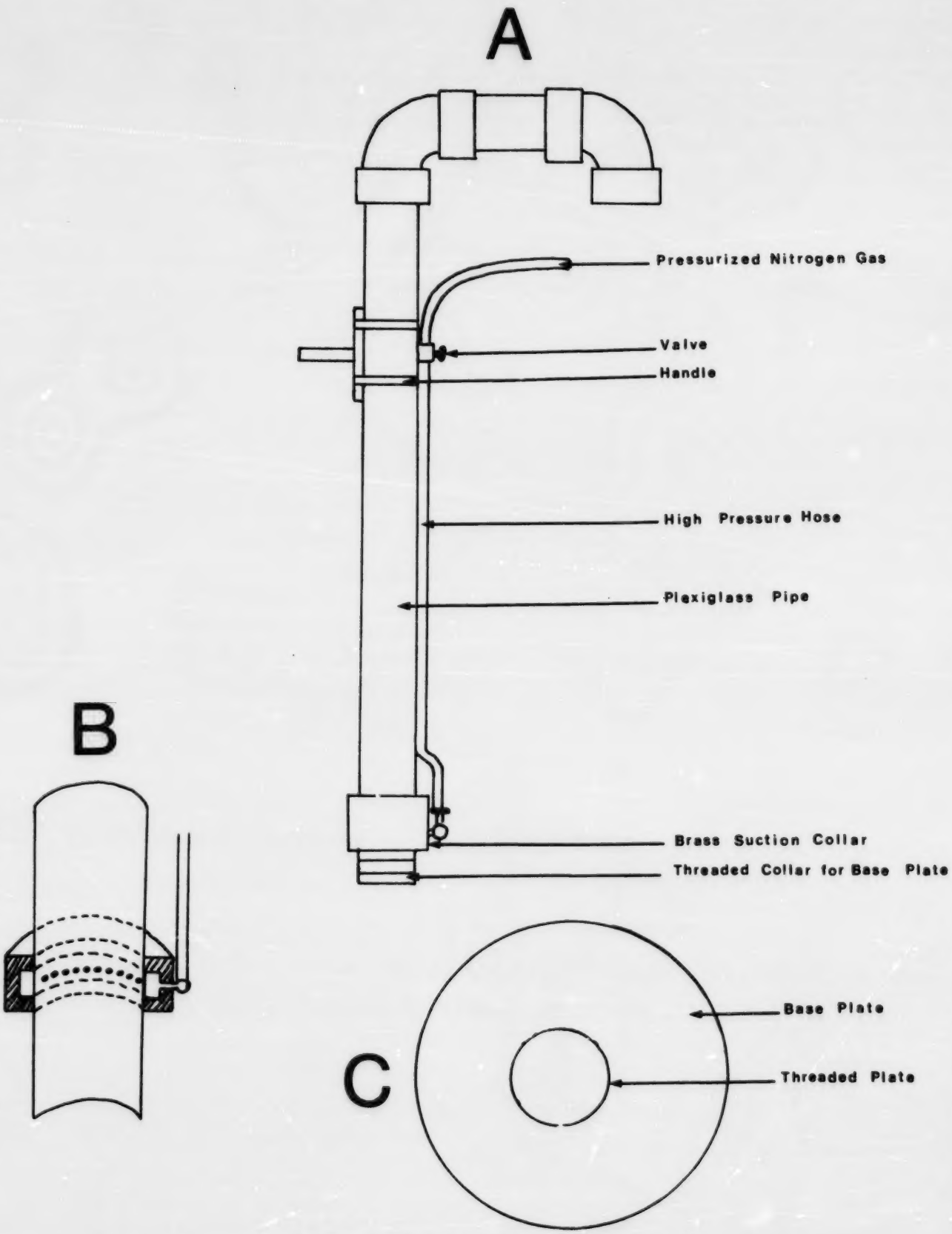


Figure 8. Air-lift sediment sampler.

(iii)Sample preservation and handling:

The water-sediment mixture was collected in 1 litre polypropylene bottles which was then transported to the laboratory as soon as possible. The clear supernatent aqueous layer was decanted and the wet sediment with minimum water content was transferred to Whirlpak® bags and stored at -20°C.

The sediment samples were thawed at room temperature, dried at ≤40°C and sieved into two fractions (i) 75-250 μm and (ii) <75 μm in grain size. The sorted size fractions were stored in polypropylene cups at room temperature tightly closed with polypropylene lids. In addition to dried sediment samples, wet sediment samples were also analyzed in order to detect the loss of mercury during the drying process, if any. Dry/wet weight ratio determination were carried out on all the sediment samples.

A total of 165 sediment samples were collected during November 5 to 20, 1981 from the four zones described as above: Zone A (35), Zone B (6), Zone C (4) and Zone D(120), the values in bracket being the number of samples collected.

(iv) Analytical methods:

Apparatus and chemistry of the method is same as that described under fish analysis section. Nearly all of the mercury in sediment is known to be inorganic mercury. Hence for all practical purposes, it is enough to determine the total mercury content.

a) Sample preparation:

Around 1 gm of wet homogenized sediment sample is aliquoted accurately into four 8 oz polypropylene cups/digestion tubes. An additional aliquot of reasonable sample size (≥5 g) is weighed out into a weighed petri dish to determine the wet/dry weight ratio. Samples are stored in the refrigerator prior to chemical analysis.

b) Sample digestion:

(1) Inorganic mercury analysis: To two of the aliquots, 10 ml of 16N H_2SO_4 was added and shaken in a water bath for 1h at 55-60^{o}C. Then the cups or tubes were taken out of the bath and cooled to room temperature. 10 ml of 6% $KMnO_4$ solution was added and the solutions were let to stand ovenight. Two hours prior to analysis, 1 ml of 5% potassium persulphate ($K_2S_2O_8$) was added and let to stand for 1.5h. Then 3 ml of 20% dextrose solution was added with stirring until the purple color disappeared. If the purple color disappeared before the addition of dextrose, the addition of $KMnO_4$ and $K_2S_2O_8$ was repeated. About 1 ml of 1% cysteine solution was added and stirred occasionally until all of the MnO_2 is reduced (variable upto several minutes). An additional 1 ml of 1% cysteine solution and 1 ml of 20% NaCl was added. The solution was made up to a known volume and analyzed the same day. If the volume was large, proper aliquot was made prior to analysis.

(2) Total mercury analysis: To the remaining two aliquots, 15 ml of digestion acid mixture (2:1 conc. H_2SO_4:HNO_3) was added under ice. The solutions were cooled well and then 2 ml of 12N HCl was added. The cups were shaken in a water bath at 60°C for 2 h. The cups were removed from the bath and cooled to room temperature. About 15 ml of 6% $KMnO_4$ solution was added cautiously with stirring and was allowed to stand for 30 min. If color disappeared, the addition of $KMnO_4$ was repeated. About 5 ml of 5% $K_2S_2O_8$ solution was added with stirring and let stand overnight. About 10 ml of hydroxylamine sulphate -- sodium chloride solution (6%) was added and mixed thoroughly until the solution was clear. The solution was made up to known volume and analyzed the same day.

d) Calibration and analysis:

Calibration of the Mercury Monitor and analysis of digested samples for inorganic and total mercury was done following the procedure described under fish analysis section (d).

e) Calculations:

Procedures described under fish analysis section (e), were followed to calculate the mercury content of the sediment samples.

2.3 Water

(i) Sampling sites:

Ongoing sample collections began in December, 1981. Initially seven sites between Edmonton and the Alberta/Saskatchewan inter-provincial border were established. They were given site numbers serially starting from the most eastern site (Figure 9).

Site #1 - Lea Park Bridge

Site #2 - Myrnam Bridge

Site #3 - Vinca (Redwater) Bridge

Site #4 - Turner Park (Fort Saskatchewan)

Site #5 - Sewage Lagoon outfall - Clover Bar

Site #6 - Beverly Bridge (Highway 16 Foot Bridge)

Site #7 - Quensel Bridge

Samples of the North Saskatchewan River water were collected from the above listed sites once a month from December, 1981 to June, 1982 and twice a month during high flow period in June, July and August, 1982. Two additional sites were added to the list in June 1982. They are Site #8 - Devon Bridge and Site #9 - Black Mud Creek (Highway #2, North Crossing) (Figure 9).

(ii) Sampling techniques:

Samples were collected using a vertical 4 litre Van Dorn bottle dropped from the deck of the above-listed bridges or by hand collecting the sample by dipping the sample bottle just below the water or ice surface whenever conditions permitted or necessitated.

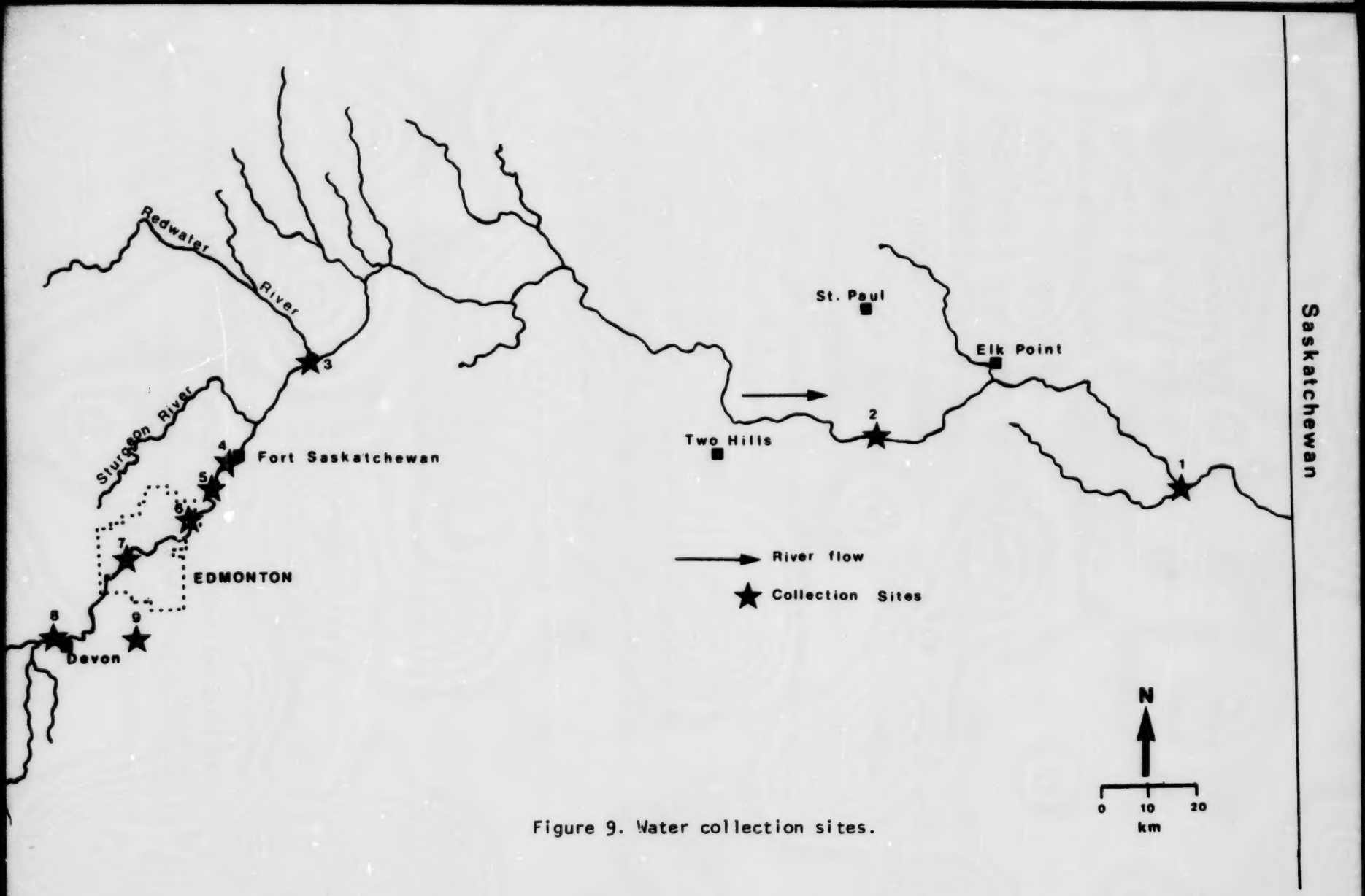


Figure 9. Water collection sites.

(iii) Sample preservation and handling:

Duplicate samples of the river water were placed in 1 litre polypropylene bottles with preservative added to the sample.

The chemical preservative was a mixture of 5 ml of conc. H_2SO_4 and 5 ml of potassium dichromate ($K_2Cr_2O_7$) added to every 1 litre of the water sample. This acid and oxidant mixture eliminates surface sorption of Hg to the container walls as well as volatilization by stabilizing all forms of Hg to the oxidized form in water. The samples were then placed in a cooler and transported to the laboratory where they were stored in an incubator or walk-in cooler at 2-4^{o}C prior to analysis.

(iv) Analytical methods:

Apparatus and chemistry of the analytical method is same as that described under fish analysis section. Almost all the detectable mercury in water is inorganic mercury. Hence the water samples were analyzed for total mercury only.

a) Sample preparation:

Exactly 15 ml of the preserved water samples was pipetted into digestor-analysis tubes. If high particulate matter was present, the sample was homogenized prior to taking an aliquot. For determining the mercury content of the particulate matter, the sample was filtered in an acid-washed all-glass apparatus. The filtrate was analyzed. The particulate matter was resuspended in distilled-deionized water and analyzed directly for its mercury content.

b) Sample digestion:

To the aliquots of water samples, 0.5 ml of conc. H_2SO_4 and 0.25 ml of conc. HNO_3 was added, followed by 0.1 ml of 6% $KMnO_4$ solution. The solutions were allowed to stand for a minimum of 15 min. If the purple color disappeared at this stage, more $KMnO_4$ solution was added till the color persisted for 15 min. Then 0.2 ml of $K_2S_2O_8$ solution was added, mixed well and left in the shaker-water bath, shaking for 2 h at 55-60°C. The tubes were then removed and cooled to room temperature. About 0.2 ml of hydroxylamine sulphate-sodium chloride solution was added to clear the solution. The samples were analyzed within 24 h.

c) Calibration, analysis and calculation:

Calibration of the mercury monitor and analysis of the digested samples for total mercury content were carried out following the procedures described under fish analysis section (d). The analyzed values represent total mercury content of the water samples.

(v) Precision and Accuracy of the Method evaluated by the Aquatic Biology Laboratory:

1. Detection Limit:

water: 0.1 ng/ml

fish: 0.2 ng/g

sediment: 0.2 ng/g

2. Recoveries from Standard Reference Materials (SPM's), 95-97% (concentration ranges 0.24 to 1.12 µg/g) of Hg in SRM's.

3. Accuracy:

Detection limit	Variation in accuracy
0.1 ng/ml (water)	± 3%
0.2 ng/g (fish & sediment)	± 5%

4. Precision:

Concentration range	Reproducibility
i) 0 - 15 ng/g	93%
ii) 15 - 37.5 ng/g	93%
iii) 37.5 - 75.0 ng/g	94%

3. RESULTS AND DISCUSSION

3.1 Sturgeon River

(i) Goldeye (Hiodon alosoides)

Methylmercury content in goldeye were between 89 to 97% and 82-99% for males and females respectively (Tables 3a and 3b). The actual concentrations were:

	Total Hg (µg/g)	Methylmercury (µg/kg)
Male Goldeye (n=17)	501 (294-1349)	471 (275-1301)
Female Goldeye (n=23)	619 (337-1555)	584 (284-1527)

Mercury content increased with and length of the fish (Figure 10). Earlier studies (Sherbin, 1979; Munson, 1978) reported total mercury levels >0.5 ppm in Goldeye.

(ii) Walleye (Stizostedion vitreum vitreum)

Methylmercury content in walleye varied from 74 to 99% of the total mercury content for both males and females (Table 4). The actual concentrations were:

	Total Hg (µg/kg)	Methylmercury (µg/kg)
Male Walleye (n=10)	643 (162-1090)	608 (120-1031)
Female Walleye (n=6)	426 (140- 836)	398 (104- 829)

Once again, mercury content increased with fish length and weight (Figure 10). Six out of ten male samples analyzed contained mercury levels >0.5 ppm and only one (out of 6) female sample showed mercury level >0.5 ppm.

Table 3a. Mercury levels (µg/kg)* in fish muscle tissue.

Species: GOLDEYE *Hiodon alosoides* Sex: MALE

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
1	35.4	0.55	48	1301	1349	96
2	34.7	0.51	72	814	886	92
3	33.6	0.48	21	322	343	94
4	26.5	0.26	37	304	341	89
5	34.8	0.57	16	484	500	97
6	31.9	0.43	30	284	314	91
7	30.7	0.40	17	403	420	96
8	34.2	0.48	19	554	573	97
9	32.9	0.49	21	364	385	95
10	35.6	0.55	29	490	519	94
11	32.2	0.50	19	275	294	94
12	31.9	0.46	22	340	362	94
13	34.5	0.48	20	470	490	96
14	34.2	0.50	26	449	475	95
15	34.7	0.57	36	381	417	91
16	31.0	0.40	33	320	353	91
17	33.1	0.46	32	447	479	93
AVERAGE	33.1	0.47	30	471	501	93.8

*expressed in wet weight for all mercury residue data in Tables 3-10

+Average moisture content is 79-82% of the total fish weight.

Table 3b. Mercury levels (µg/kg) in fish muscle tissue

Species: GOLDEYE *Hiodon alosoides* Sex: FEMALE

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
1	34.9	0.64	24	594	618	96
2	33.1	0.54	44	464	508	91
3	37.8	0.51	28	626	654	96
4	32.4	0.59	24	397	421	94
5	38.4	0.60	24	558	582	96
6	34.5	0.55	18	324	342	95
7	38.3	0.66	9	568	577	98
8	35.2	0.66	25	342	367	93
9	33.9	0.60	21	414	435	95
10	33.6	0.56	29	427	456	94
11	36.9	0.72	27	706	733	96
12	36.6	0.70	8	624	632	99
13	33.6	0.56	39	453	492	92
14	35.5	0.64	43	357	400	89
15	36.3	0.64	68	315	383	82
16	36.9	0.62	54	668	722	93
17	34.7	0.62	54	633	687	92
18	36.9	0.74	77	875	952	92
19	36.4	0.78	40	561	601	93
20	36.9	0.76	17	407	424	96
21	38.5	0.82	34	1307	1341	98
22	38.1	0.68	28	1527	1555	98
23	33.0	0.54	53	284	337	84
AVERAGE	35.8	0.64	35	584	619	93.6

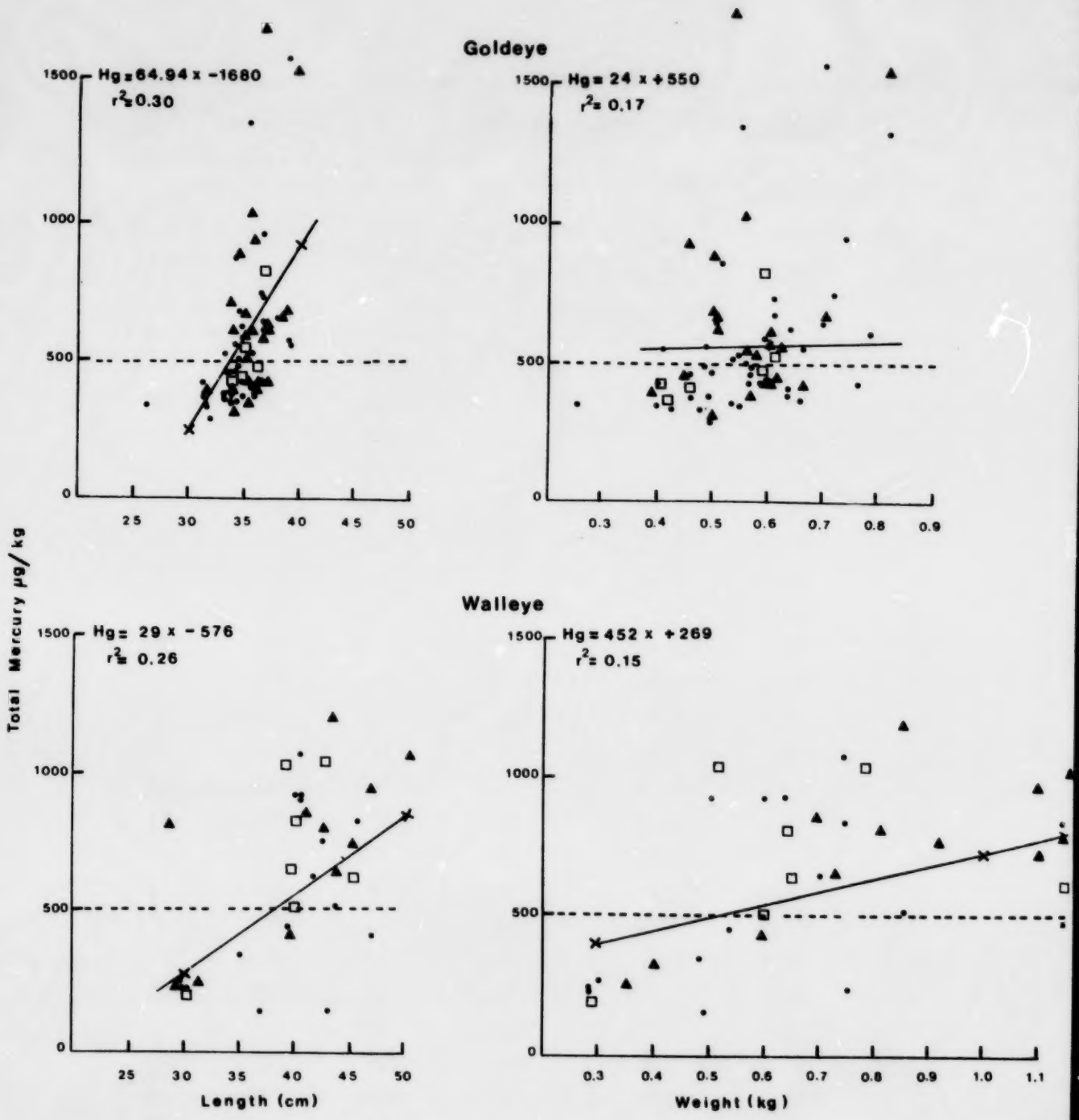
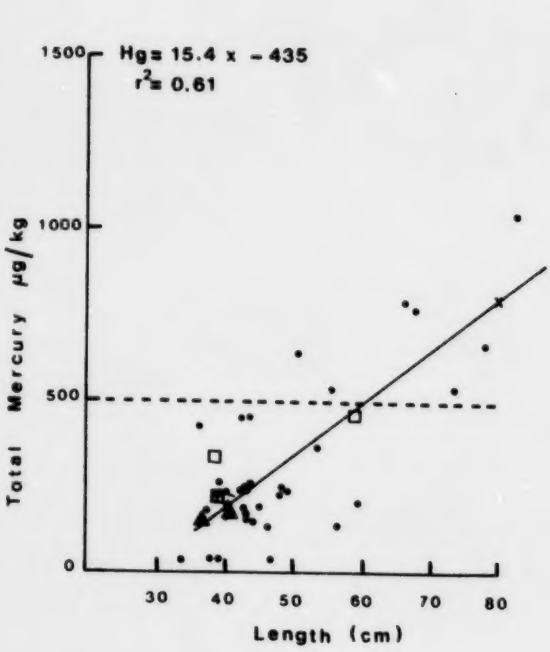


Figure 10. Concentration of total mercury in goldeye, walleye and pike of different length and weight collected from the North Saskatchewan River at the Sturgeon River (•), Myrnam (□) and Lea Park (▲) sites.



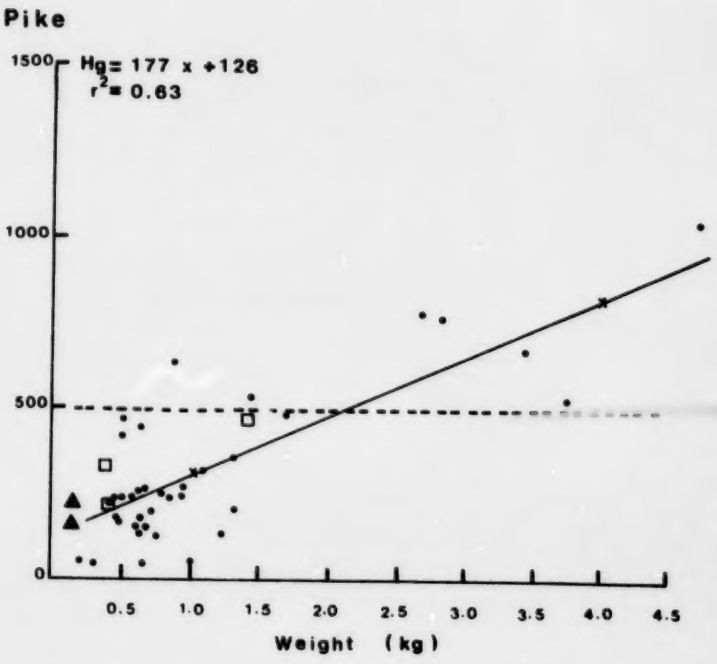


Figure 10 (continued).

(iii)Sauger (Stizostedion canadense)

Only four samples (2 male and 2 female) were collected and analyzed for mercury levels (Table 5). The percent methyl mercury was 71-96 of the total mercury and females contained higher total mercury residues than male exceeding >0.5 ppm.

(iv) Northern Pike (Esox lucius)

The analytical results for mercury levels in northern pike are presented in Tables 6a and 6b. The mercury levels were:

	Total Hg (µg/kg)	Methylmercury (µg/kg)
Male Northern Pike (n=25)	266 (44- 629)	236(3- 602)
Female Northern Pike (n=14)	401 (47-1039)	373 (31-1003)

The percent methylmercury content was 71-98 and 37-98 of the total mercury for males and females respectively. Once again there was a significant correlation between mercury content and the body weight and length (Figure 10). The average total mercury content was 0.266 ppm (male, n=25) and 0.402 ppm (females, n=14) respectively.

(v) Longnose Sucker (Catostomus catostomus)

Only seven samples of each male and female Longnose Sucker species were collected and the results are given in Tables 7. The mercury concentrations were:

	Total Hg (µg/kg)	Methylmercury (µg/kg)
Male Longnose Sucker (n=7)	118-212	84-169
Female Longnose Sucker (n-7)	62-282	47-253

The methylmercury content ranged from 71-88% for males and 74-94% for females respectively. The average total mercury content was 0.163 ppm for males (n=7) and 0.173 ppm for females (n=7) respectively.

Table 4. Mercury levels (µg/kg) in fish muscle tissue.

Species: WALLEYE *Stizostedion vitreum vitreum*

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	%Methyl Hg
			MALE			
1	37.1	0.50	42	120	162	74
2	41.3	0.75	59	1031	1090	95
3	38.2	0.54	34	422	456	93
4	41.2	0.52	40	874	914	96
5	39.9	0.61	19	910	929	98
6	42.0	0.72	47	602	649	93
7	40.3	0.64	7	919	926	99
8	42.5	0.75	21	757	778	97
9	29.0	0.31	32	245	277	89
10	29.7	0.28	45	201	246	82
AVERAGE	38.1	0.56	35	608	643	91.6
			FEMALE			
1	43.0	0.77	36	104	140	74
2	43.5	0.86	42	476	518	92
3	45.6	1.16	7	829	836	99
4	30.1	0.28	12	227	239	95
5	35.3	0.49	20	320	340	94
6	47.0	1.18	50	431	481	90
AVERAGE	40.8	0.79	28	398	426	90.6

Table 5. Mercury levels (µg/kg) in fish muscle tissue.
Species: SAUGER *Stizostedion canadense* Sex: MALE (samples 1 & 2)
FEMALE (samples 3 & 4)

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
1	32.8	0.35	79	192	271	71
2	31.9	0.36	33	669	702	95
3	34.4	0.44	22	530	552	96
4	33.8	0.44	30	809	839	96
AVERAGE	33.2	0.40	41	550	591	89.5

Table 6a. Mercury levels (µg/kg) in fish muscle tissue.
Species: NORTHERN PIKE Esox lucius Sex: MALE

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
1	43.3	0.60	50	210	260	81
2	43.3	0.60	56	198	254	78
3	55.5	1.40	26	511	537	95
4	35.9	0.52	30	380	410	93
5	37.1	0.36	20	152	172	88
6	38.3	0.44	10	38	48	79
7	34.5	0.31	13	31	44	71
8	55.6	1.22	20	104	124	84
9	58.9	1.27	13	187	200	94
10	29.6	0.20	49	3	52	6
11	50.2	0.83	27	602	629	96
12	44.6	0.63	35	241	276	87
13	42.3	0.51	5	237	242	98
14	48.6	0.91	39	211	250	84
15	42.4	0.58	30	151	181	83
16	45.3	0.62	24	175	199	88
17	43.3	0.61	12	140	152	92
18	40.9	0.51	28	218	246	89
19	60.4	1.70	23	475	498	95
20	51.4	1.05	24	277	301	92
21	39.9	0.46	33	234	267	88
22	42.0	0.50	27	446	473	94
23	42.5	0.61	22	129	151	85
24	44.4	0.60	51	413	464	89
25	39.6	0.47	20	199	219	91
AVERAGE	44.4	0.7	27.5	238.5	266.0	84.8

Table 6b. Mercury levels (µg/kg) in fish muscle tissue.
Species: NORTHERN PIKE Esox lucius Sex: FEMALE

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
1	44.4	0.59	90	52	142	37
2	46.0	0.68	16	31	47	66
3	40.9	0.49	14	209	223	94
4	53.9	1.29	56	330	386	86
5	40.3	0.48	6	192	198	97
6	46.3	0.75	10	106	116	91
7	49.1	0.77	28	222	250	89
8	67.8	2.82	40	737	777	95
9	66.8	2.42	14	782	796	98
10	82.7	4.75	36	1003	1039	97
11	47.2	0.82	30	212	242	88
12	73.7	3.72	21	518	539	96
13	77.3	3.45	20	664	684	97
14	40.0	0.49	20	161	181	89
AVERAGE	55.5	1.68	28.6	372.8	401.4	87

(vi) Northern Redhorse Sucker (Moxostoma macrolepidotum)

The mercury concentrations were:

	Total Hg (µg/kg)	Methylmercury (µg/kg)
Male Northern Redhorse Sucker (n=4)	304-368	255-335
Female Northern Redhorse Sucker (n=9)	272-619	249-550

(Table 8)

The methylmercuy content was 77-94% for males and 89-94% for females respectively. The average total mercury concentration was 0.336 ppm for males (n=4) and 0.432 ppm for females (n=9) respectively.

(vii) (a) Quillback Sucker (Caproides cyprinus)

(b) Burbot (Lota lota)

Table 9 presents the values for mercury concentration in these two species (one sample each). Total mercury content of 433 and 395 µg/kg and 90 and 78% of it in the methylmercury form were determined for Quillback Sucker and Burbot respectively.

(viii) White Sucker (Catostomus commersoni)

The mercury concentrations were (Table 10):

	Total Hg (µg/kg)	Methylmercury (µg/kg)
Male White Sucker (n=9)	28-556	16-537
Female White Sucker (n=12)	128-659	72-624

The methylmercury content varied from 57 to 100% of the total mercury for males and 56 to 96% for females. The average total mercury concentrations were 0.273 ppm for males (n=9) and 0.314 ppm for females (n=12) respectively.

Table 7. Mercury levels (µg/kg) in fish muscle tissue.

Species: LONGNOSE SUCKER Catostomus catostomus

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALES			
1	41.8	1.32	19	132	151	87
2	41.6	1.19	33	163	196	83
3	37.6	0.79	34	84	118	71
4	40.9	1.11	26	107	133	81
5	40.2	1.04	31	169	200	85
6	39.9	1.60	16	115	131	88
7	40.7	0.96	41	171	212	81
AVERAGE	40.4	1.14	28.6	134.4	163	82.3
			FEMALE			
1	44.3	1.40	17	135	152	89
2	43.8	1.45	73	209	282	74
3	45.0	1.37	36	111	147	76
4	41.1	1.10	14	95	109	87
5	45.9	1.60	17	253	270	94
6	43.7	1.24	15	47	62	76
7	44.5	1.44	20	171	191	90
AVERAGE	44.0	1.37	47	145.9	173.3	83.7

Table 8. Mercury levels (µg/kg) in fish muscle tissue.
Species: NORTHERN REDHORSE SUCKER *Moxostoma macrolepidotum*

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	37.2	0.82	85	283	368	77
2	36.9	0.79	20	335	355	94
3	38.1	0.90	61	255	316	81
4	35.3	0.80	44	260	304	86
AVERAGE	36.9	0.83	52.5	283.3	335.8	84.5
			FEMALE			
1	39.2	1.18	46	383	429	89
2	44.6	1.48	42	545	587	93
3	37.6	1.00	34	281	315	89
4	39.3	0.99	50	337	367	92
5	38.8	1.07	41	385	426	90
6	35.8	0.92	69	550	619	89
7	38.8	0.98	22	369	391	94
8	39.3	1.00	23	249	272	92
9	38.5	1.12	29	458	487	94
AVERAGE	39.1	1.08	37.3	395.2	432.6	91.3

Table 9. Mercury levels (µg/kg) in fish muscle tissue.

Species: QUILLBACK SUCKER *Capriodes cyprinus* Sex: MALE

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
1	35.2	0.94	43	390	433	90

Species: BURBOT *Lota lota* Sex: MALE

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
1	60.2	1.20	89	306	395	78

Table 10. Mercury levels (µg/kg) in fish muscle tissue.
Species: WHITE SUCKER Catostomus commersoni

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	32.1	0.58	12	16	28	56
2	39.5	0.95	--	58	58	100
3	39.3	1.10	36	195	231	84
4	39.7	1.03	19	537	556	97
5	35.9	0.80	16	152	168	91
6	40.2	0.92	19	339	358	95
7	38.0	0.90	28	219	247	89
8	40.5	1.06	25	375	400	94
9	43.8	1.27	18	389	407	96
AVERAGE	38.7	0.96	21.6	253.3	272.6	89.1
			FEMALE			
1	43.6	1.48	35	372	407	91
2	43.6	1.38	44	186	230	81
3	43.7	1.41	33	210	243	86
4	42.6	1.20	19	249	268	93
5	42.9	1.20	35	624	659	95
6	29.0	0.39	38	90	128	70
7	46.1	1.38	57	492	549	90
8	36.1	0.84	56	72	128	56
9	39.3	1.09	29	232	261	89
10	42.0	1.17	31	233	264	88
11	43.1	1.31	43	156	199	78
12	43.7	1.55	18	410	428	96
AVERAGE	41.2	1.2	36.5	277.2	313.7	84.4

In general, mercury levels were relatively higher in migratory fish species such as Goldeye, Walleye and Sauger. The female seem to contain higher mercury residues than the corresponding male species. It is likely that the mercury in the migratory species orginate from Saskatchewan section of the river.

3.2 Myrnam and Lea Park

Mercury residues in fish from the Myrnam and Lea Park areas were generally similar to those recorded near the Sturgeon River [Figure 10; Tables 11-23]. This would be expected considering that most of the species are migratory, thereby encouraging mixing of stocks. In addition, as indicated in Tables 24-26, mercury concentrations in sediments were similar throughout the study area. Consequently, exposure to mercury would also be similar.

Consumption Limits

In Canada the maximum limit for total mercury in fish is 0.5 mg/kg regardless of frequency of consumption whereas in Sweden, Finland and several other countries, the limit is 1.0 mg/kg. The Maximum Tolerable Weekly Intake for adults is generally considered to be 0.25 mg for a 50 kg adult. Since the average concentration of total mercury in goldeye was 569 µg/kg, ~440 g (~16 oz) of flesh can be consumed per week. This provides for a safety limit of 50 times based on laboratory toxicity work. Almost all of the goldeye collected from the river fall

Table 11. Mercury levels (µg/kg) in fish muscle tissue.

Species: GOLDEYE *Hiodon alosoides* Site: Myrnam

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	34.6	0.54	68	361	429	84
2	33.4	0.43	96	228	324	70
3	34.2	0.45	100	341	441	77
4	36.6	0.57	84	734	818	90
AVERAGE	34.7	0.50	87	438	503	80
			FEMALE			
1	35.7	0.62	70	447	517	87
2	36.2	0.58	68	416	484	86
AVERAGE	36.0	0.60	69	431	500	86

Table 12. Mercury levels (µg/kg) in fish muscle tissue.
Species: WALLEYE *Stizostedion vitreum virtreum*. Site: Myrnam

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	39.8	0.63	73	756	829	91
2	39.7	0.65	40	609	649	94
3	42.4	0.78	61	972	1033	94
4	45.5	1.3	77	527	604	87
5	38.4	0.52	32	1002	1034	97
6	40.1	0.60	52	454	506	90
7	30.4	0.28	50	149	199	75
AVERAGE	39.5	0.68	55	638	693	90

Table 13. Mercury levels (µg/kg) in fish muscle tissue.
Species: SAUGER Stizostedion canadense Site: Myrnam

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	40.7	0.62	44	658	702	94
2	30.8	0.28	79	513	592	87
3	31.4	0.25	54	601	655	92
4	28.4	0.20	63	563	626	90
AVERAGE	32.8	0.34	60	584	644	91
			FEMALE			
1	38.9	0.56	69	727	796	91
2	40.1	0.58	42	583	625	93
3	39.0	0.61	62	771	833	93
4	36.2	0.44	57	587	644	91
5	37.2	0.50	57	524	581	90
6	38.8	0.51	50	875	925	95
7	30.0	0.23	84	614	698	88
AVERAGE	37.2	0.49	60	669	729	92

Table 14. Mercury levels (µg/kg) in fish muscle tissue.
Species: NORTHERN PIKE Esox lucius Site: Myrnam

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	38.3	0.38	85	278	363	77
2	38.0	0.41	23	201	224	90
AVERAGE	38.1	0.39	0.45	239	294	84
			FEMALE			
1	59.3	1.42	57	424	481	88

Table 15. Mercury levels (µg/kg) in fish muscle tissue.
Species: NORTHERN REDHORSE SUCKER Moxostoma macrolepidotum Site: Myrnam

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	35.7	0.71	58	334	392	85
2	39.8	1.19	40	419	459	91
AVERAGE	37.8	0.94	49	377	426	88

Table 16. Mercury levels (µg/kg) in fish muscle tissue.
Species: LONGNOSE SUCKER Catostomus catostomus Site: Myrnam

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	41.6	1.03	26	287	313	92
2	42.5	1.16	86	319	405	79
3	37.6	0.88	43	185	228	81
4	40.5	0.98	70	251	321	78
5	42.7	1.17	71	145	216	67
6	40.3	0.82	67	198	265	75
7	40.9	0.98	71	290	361	80
8	39.5	0.96	51	164	215	76
AVERAGE	32.5	1.00	61	230	291	79
			FEMALE			
1	42.0	1.1	67	158	225	70
2	42.9	1.17	61	353	414	85
AVERAGE	42.4	1.13	64	256	320	77

Table 17. Mercury levels (µg/kg) in fish muscle tissue.
Species: WHITE SUCKER *Catostomus commersoni* Site: Myrnam

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	38.4	0.95	80	175	255	69
2	37.5	1.11	90	428	518	83
3	38.7	1.08	44	305	349	87
4	41.5	1.14	77	298	375	80
AVERAGE	39.0	1.07	73	301	374	80
			FEMALE			
1	41.5	1.33	68	323	391	83
2	42.5	1.18	100	235	335	70
AVERAGE	42.0	1.25	132	279	363	76

Table 18. Mercury levels (µg/kg) in fish muscle tissue.
Species: GOLDEYE *Hiodon alosoides* Site: Lea Park

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	34.0	0.51	30	640	699	92
2	35.1	0.50	51	622	673	92
3	35.6	0.52	44	588	632	93
4	34.6	0.52	45	821	866	95
5	32.9	0.44	43	401	444	90
6	35.4	0.57	46	485	531	91
7	35.4	0.56	38	342	380	90
8	36.7	0.60	61	514	575	89
9	34.1	0.49	35	264	299	88
10	30.6	0.38	49	332	381	87
11	35.9	0.56	67	950	1017	93
12	35.3	0.45	45	875	920	95
13	37.9	0.62	48	501	549	91
AVERAGE	34.9	0.52	46	564	613	91
			FEMALE			
1	35.0	0.62	35	405	440	92
2	35.4	0.59	41	395	436	91
3	38.3	0.70	47	603	650	93
4	37.1	0.61	61	536	597	90
5	37.2	0.57	43	479	522	92
6	35.2	0.58	38	449	487	92
7	36.2	0.53	63	1703	1766	96
8	37.0	0.66	53	353	406	87
9	39.2	0.79	46	1509	1555	97
10	34.8	0.58	44	380	424	90
AVERAGE	36.5	0.62	47	681	728	92

Table 19. Mercury levels (µg/kg) in fish muscle tissue.
Species: WALLEYE *Stizostedion vitreum vitreum* Site: Lea Park

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	50.6	1.30	51	964	1015	95
2	42.7	0.82	44	756	800	95
3	43.1	0.85	43	1159	1202	96
4	40.7	0.68	62	783	845	93
5	45.2	0.92	66	693	759	91
6	29.3	0.39	96	222	318	70
7	30.6	0.35	73	183	256	72
AVERAGE	40.3	0.76	62	680	742	87
			FEMALE			
1	39.4	0.58	63	363	426	85
2	27.9	1.20	63	747	810	92
3	46.2	1.08	83	842	925	91
4	43.5	0.72	60	593	652	91
5	43.8	1.10	55	663	718	92
AVERAGE	40.1	0.94	65	642	706	90

Table 20. Mercury levels (µg/kg) in fish muscle tissue.
Species: SAUGER Stizostedion canadense Site: Lea Park

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	37.7	0.49	64	853	917	93
2	30.3	0.25	41	625	666	94
3	38.1	0.50	52	1533	1585	97
4	35.9	0.41	59	762	821	93
5	25.7	0.19	44	333	377	88
6	32.4	0.32	111	652	763	86
7	33.6	0.38	105	664	769	86
AVERAGE	33.4	0.36	68	775	843	91
			FEMALE			
1	35.9	0.50	30	807	837	96
2	38.9	0.54	37	926	963	96
3	35.6	0.47	62	662	724	91
4	33.7	0.40	77	788	865	91
AVERAGE	36.0	0.48	52	796	847	94

Table 21. Mercury levels (µg/kg) in fish muscle tissue.
Species: NORTHERN PIKE Esox lucius Site: Lea Park

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	38.1	0.38	53	185	238	78
2	36.7	0.32	40	218	258	85
AVERAGE	35.9	0.35	46	201	248	81

Table 22. Mercury levels (µg/kg) in fish muscle tissue.
Species:NORTHERN REDHORSE SUCKER Moxostoma macrolepidotum Site:Lea Park

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	37.7	0.85	36	285	321	89
2	36.1	0.75	37	250	287	87
AVERAGE	36.8	0.80	36	267	304	88
			FEMALE			
1	39.7	0.88	103	109	212	51
2	34.5	0.62	43	124	167	74
3	38.7	0.88	56	303	359	84
4	34.3	0.61	39	228	267	85
5	39.1	1.10	50	245	295	83
6	36.2	0.85	60	413	473	87
AVERAGE	37.1	0.82	59	237	300	77

Table 23. Mercury levels (µg/kg) in fish muscle tissue.
Species: LONGNOSE SUCKER Catostomus catostomus Site: Lea Park

Sample Number	Length (cm)	Weight (kg)	Inorganic Hg	Methyl Hg	Total Hg	% Methyl Hg
			MALE			
1	40.0	0.84	86	158	244	65
2	39.6	0.87	112	295	407	73
3	23.4	0.18	81	30	111	27
4	39.4	0.89	40	120	160	75
5	35.1	0.58	33	221	254	87
6	39.0	0.85	47	192	239	80
7	41.2	1.05	35	322	357	90
8	38.3	0.83	38	320	358	89
AVERAGE	37.0	0.76	59	207	266	73
			FEMALE			
1	44.2	1.30	41	210	251	84
2	41.8	0.99	43	135	178	76
3	45.6	1.33	68	323	391	83
4	41.1	0.95	60	176	236	75
5	39.5	0.88	67	124	191	65
6	40.6	0.88	111	107	218	49
7	39.5	0.74	98	143	241	59
8	39.4	0.95	112	185	297	62
9	42.0	0.94	80	130	210	62
10	42.1	1.30	83	150	233	64
11	38.1	0.74	75	114	189	60
12	43.6	1.18	49	499	548	81
13	43.8	1.25	46	295	341	87
14	40.2	0.83	87	196	283	69
AVERAGE	41.5	1.02	73	199	272	64

with the length range 30-40 cm. Consequently consumption standards based on different size fish are not needed. Walleye >35 cm in length are likely to contain mercury levels in excess of 0.5 mg/kg. Using the average residue for fish in this category (0.65 mg/kg) gives a maximum weekly intake of ~350 g or 13 oz. No consumption limits need to be placed on fish <35 cm. Nothern pike exceed the 0.5 mg/kg at a length of 60 cm. Since the average mercury concentration in this size class in 0.65 mg/kg, the maximum weekly intake is ~380 g or 13 oz. Once again, no limits need to be placed on fish <60 cm.

In all instances, pregnant women should not eat fish from the river, reflecting the increased sensitivity of the developing fetus to mercurials (see summary).

Although not normally consumed mercury residues in the sucker species were generally <0.5 mg/kg. These fish are therefore considered safe to eat by adults.

Sediment:

The results of mercury analysis in sediments collected from the North Saskatchewan River are presented in Tables 24-26. The river was divided into four major sections (A,B,C and D) based on the discharge patterns. The total mercury values (µg/kg dry weight) were:

Zone	A	B	C	D
Mean	53	75	106	92
95% confidence limits	±13.6	±38.6	±21.5	±16.0
Range	8 - 173	20 - 157	80 - 124	13 - 335
N	35	6	4	63

Slight elevations in the mean values in Zone B and C compared to Zone A indicate the possible low level input of municipal and industrial effluent discharges along the North Saskatchewan River. However, almost comparable mean values between Zones C and D suggest that Zone D (from Redwater to Alberta/Saskatchewan border) receives a constant load from non-point sources such as agricultural runoffs.

Although there is an extensive but low level of mercury in the North Saskatchewan River, the relatively higher mercury levels in the migratory fish species could possibly originate from Saskatchewan. Further studies on the migratory pattern, extent of migration, energetics involved in the process and associated metabolic changes of

Table 24. Total Mercury levels (µg/kg dry weight) in sediments from North Saskatchewan River

Zone A

Sample No.	Mercury Content	Sample No.	Mercury Content	Sample No.	Mercury Content
1	22	13	42	25	54
2	10	14	62	26	55
3	11	15	54	27	91
4	21	16	51	28	35
5	10	17	83	29	42
6	14	18	114	30	104
7	10	19	32	31	59
8	19	20	96	32	100
9	10	21	51	33	78
10	13	22	41	34	115
11	75	23	63	35	173
12	45	24	8		

Mean: 53

Range: 8 - 173

Table 25. Total Mercury levels (µg/kg dry weight) in sediments from North Saskatchewan River

Zones B and C

Sample Number	Mercury Content	
1	40	
2	87	
3	76	Zone B
4	157	
5	67	
6	20	
7	124	
8	80	Zone C
9	103	
10	115	

Zone B Mean: 75, Range: 20 - 157

Zone C Mean:106, Range: 80 - 124

Table 26. Total Mercury levels (µg/kg dry weight) in sediments from North Saskatchewan River.

Zone D

Sample No.	Mercury Content	Sample No.	Mercury Content	Sample No.	Mercury Content
1	29	22	65	43	146
2	64	23	64	44	335
3	58	24	73	45	75
4	80	25	64	46	76
5	110	26	51	47	75
6	112	27	69	48	107
7	88	28	77	49	122
8	262	29	58	50	232
9	89	30	42	51	152
10	59	31	46	52	41
11	51	32	46	53	13
12	99	33	71	54	154
13	138	34	22	55	128
14	66	35	57	56	99
15	81	36	25	57	108
16	64	37	60	58	92
17	68	38	102	59	55
18	63	39	173	60	65
29	57	40	76	61	16
20	73	41	64	62	154
21	296	42	127	63	116

Mean: 92

Range: 13 - 335

the fish have to be initiated for proper evaluation of the origin of mercury in these fish species.

Water:

The results of total mercury analysis in water samples collected along the North Saskatchewan River are given in Table 27. A total of nine sampling sites were chosen along the river. The upstream values (Blackmud Creek and Devon) are ~ 0.06 µg/L of total mercury and elevate near industrial discharge sites (Cloverbar, Fort Saskatchewan sites). In general, spring runoffs seem to elevate the mercury levels in water (Table 27; April 82 sampling dates). It was interesting to note that the mercury levels in water dropped to background values of ~ 0.03 µg/L in August, independent of the site. It will be interesting to determine the suspended solid load and the mercury associated with it.

Table 27. Total Mercury Levels (µg/l) in unfiltered water samples.

Date	Blackmud Creek	Devon	Quensel Bridge	Cloverbar Bridge	Cloverbar Sewage	Fort. Sask.	Red Water	Myrnam Bridge	Lea Park
Dec 8-9, 81	---	---	0.60 1.58	0.25	---	0.25	0.39 1.22	0.25	0.34 0.23
Jan 22, 82	---	---	0.03 0.03	0.10 0.07	0.07 0.05	---	0.23	0.03	0.11
Feb 12, 82	---	---	0.17	0.27	0.36 0.2	---	0.30	0.36 0.15	0.03
March 13, 82	---	---	0.18	0.15	---	0.07 0.03	0.05	---	---
April 20, 82	---	---	0.89 0.42	0.65 0.29 0.33	---	0.30	0.15	0.44 0.43	0.16
May 31, 82	---	---	0.03	0.16	0.31	0.01	0.07	0.07	0.05
June 17-18, 82	0.04	0.04	0.04	0.20	0.80 0.06	0.07	0.07	0.17 0.65 0.35	0.05
July 2, 82	0.06	0.07	0.08	0.05	0.13	---	0.08	0.06	0.04
July 19-20, 82	0.06	0.07	0.05	0.09	0.07	0.07	0.05	0.10	0.11
Aug 4, 82	0.06	0.50	0.13	0.17	0.34	0.06	0.06	0.05	0.13
Aug 20, 82	0.02	0.02	0.03	0.02	0.03	0.02 0.03	0.02	0.04 ---	0.03 ---
Sept. 13, 82	0.17 0.17	0.22	0.15	0.08	0.20	0.18	0.29	0.09	0.26 0.50
Oct. 26, 82	0.10 0.12	0.59	0.34	0.11	0.20	0.29	0.14	0.14	0.63

- = Samples not collected

4.0 TOXICOLOGICAL CONSIDERATIONS IN EXPOSURE ASSESSMENT OF MERCURIALS

For toxicological evaluations, mercurials are classified into (i) elemental mercury (ii) inorganic mercury compounds (iii) short-chain alkyl mercurials (R=methyl or ethyl) and (iv) other organomercurials (R=aryl or alkyl >ethyl) (Suzuki, 1979). The human genetic code evolved in a period ancient to the modern environmental pollutants and heavy metals have not provided the protective barriers against their penetration and toxic action. Experimental studies (Jugo, 1977) have shown that many heavy metals enter the human body via the gastrointestinal tract and more so in young organisms. The vast difference in barrier permeability of the forms of the heavy metals constitute a sericus health threat to humans, especially greatly disturbed immunological system in infants. The protective mechanisms that are commonly existing in adults include excretion, binding to blind sites (sites with no specific function), inactivation by metallothioneins and biotransformation into less toxic forms. It has been speculated that growing organisms have lower capacity for metallothionein synthesis (Jugo, 1976). Studies in this area of toxicology is in an infant stage and future studies must devote to the understanding of the vulnerability of organisms at different life-stages to the environmental pollutants.

In general, gastrointestinal absorption of inorganic mercury is low (~7%) compared to methylmercury (>90%) (Berglund and Berlin, 1969). Growing organisms absorb all heavy metals including mercury in greater amounts than adults. Mercury possesses a strong affinity for kidney tissues and liver tissues bound to metallothioniens, a low molecular

weight (6000-10,000 MW) protein containing sulphydryl groups. The transport and translocation of mercury between tissues is linked very much with the type and content of the metal-binding proteins. Further work in this area should emphasize the need for standardizing the experimental conditions, such as age and species of the animal, route and speciation of the mercury administered and then determine their ability to produce metallothionein as a response. Based on existing literature evidence, the current standards for allowable daily inorganic mercury and other heavy metals exposure to children must be reexamined. Though the growing organism is more resistant to the lethal action of mercury, it is greatly outweighed by the higher permeability across gastrointestinal barrier, lower excretion and unfavourable partitioning among tissues.

Methylmercury, as opposed to inorganic mercury, crosses the gastrointestinal barrier to the same extent (>90%) in both young and adult organisms. Methylmercury is more slowly reduced than other organomercurials. This, combined with the low excretion rate (biological half life for humans = 70 days), makes it a cumulative toxic substance. Placental movement of methylmercury is ten times greater than that of inorganic mercury and dose-dependent. Methyl mercury accumulates in both cerebral cortex and cerebellum. After diffusing rapidly across the cell membrane, it quickly binds to sulphydryl groups inside the cell, inhibiting protein synthesis (Yoshino et al, 1966) and RNA synthesis (Chang et al, 1972 a,b). The neurological disorders due to exposure to toxic levels of methylmercury are well documented in literature. From the public health point of view, subtle effects such as behavioural and intellectual deficiencies due to long-term exposure

to methylmercury is of great concern, because they are difficult to detect at the early stages (Jugo, 1979).

The toxicity of mercurials is determined by:

(i) chemical form at entry

(ii) route of entry

(iii) body burden - dose relationship

(iv) presence of chelators and their effect on the form and properties of the mercurials and

(v) rate of transport

Environmental interactions as well as chemical changes within the organism contribute to the above processes. The toxic effect of mercury can be antagonized or synergized by alteration of the strength of binding between mercury and the binding sites of the biomolecules which are vital to the organs. (Magos and Webb, 1979). Selenium is known to interact antagonistically with mercury. Flesh of some ocean fish is reported to contain more selenium than mercury on a molar basis (Ganther et al, 1972; Koeman et al, 1973). If this is true in other fish species, this might mean that methylmercury is in a detoxified form. Knowledge on this area of antagonism and synergism is scanty; possible explanations are, shift in the binding sites (from essential to non-essential in the former case) and/or relocalization among body regions. Low molecular weight metalloproteins, high in cysteine content are known to accumulate heavy metals. These proteins have been isolated from human kidney and liver and kidney of several animals. The role of metalloproteins, especially metallothionein as a natural detoxicant of heavy metals and their level in the fish body as a response to chemical stress should be investigated in detail. This could possibly develop

into a monitoring tool to assess the chemical stress even when the toxicants are not analytically detectable in the water body. Also the alleged inefficiency of metallothionein in detoxifying methylmercury based on the binding sequences $Hg^{2+}>Cd^{2+}>>CH_3Hg^+$ should be investigated. A few demethylating bacteria have been identified (Bartlett et al, 1977; Furakawa et al, 1969). Ramamoorthy et al. (1982) reported recently that (i) growing bacterial cells transform inorganic and methylmercury to the volatile form and (ii) living but non-growing bacterial and algal cells demethylate CH_3Hg to inorganic Hg^{2+}. This combined with chemical breakdown of CH_3Hg during cooking of fish might yield much less toxic form of mercury, namely Hg^{2+}, capable of being sequestered strongly by metallothionein. Further studies in this area will provide much needed information on the stability of CH_3Hg in the aquatic environment. These observations suggest that for meaningful survey of methylmercury the samples should be stored properly and analyzed with minimum storage time.

To sum up, mercuric compounds have no known normal metabolic functions and hence their presence in living organisms indicates the contamination from natural and/or anthropogenic sources. Developing organisms are more vulnerable to the toxic action of methylmercury. Differences in toxicities of mercury compounds could arise from the varying permeabilities depending on the bound ligand. Low excretion of mercurials are due to their unfavourable partitioning among the body ligands. Future studies should concentrate on the specifities of mercury speciation in aqueous system and their toxicities in order to determine safe permissive daily exposures to mercurials. This task is extremely difficult since toxicological studies are done on experimental

animals and extrapolation to humans becomes complicated due to interspecies differences, variation in individual response among humans. The exposure level should take into consideration the long-term effects from low level chronic exposures of mercury. From the available literature evidence on the placental transfer of mercury, pregnant women should exercise caution in consuming mercury-contaminated fish diet. A limit of 0.25μg/g of methyl mercury consumption has been proposed for pregnant women (Kahn, 1971). The acceptable daily intake of methyl mercury suggested by the FAO/WHO, Expert Committee on Food Additive Evaluation in the sixteenth report (1972) is 0.2 mg of Hg per adult person of 70 kg body weight per week. Based on this, an acceptable daily intake of 25μg methylmercury per day can be calculated for a 60 kg woman (Khera, 1979). Although this might be safe for the mother, it does not consider the risk of the increased sensitivity of the developing fetus to the mercurials.

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POOR

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